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THE MECHANISM OF NITROGEN UTILIZATION BY AZOTOBACTER

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The nitrogen molecule is very inactive, and considerable energy is required to make it reactive, since the two atoms in N_2 are combined very strongly. But when the two atoms of nitrogen are separated and combined with other elements they are very active. In an investigation of the mechanism of nitrogen fixation by Azotobacter, the primary question that arises is how the bacteria first combine with the free nitrogen. In answer to this question, many explanations have been given. These may be divided into three main groups, as follows:

The theory of the direct combination of the nitrogen with certain organic compounds in the cells of the bacteria. This is difficult to prove by experiment.

The oxidation theory. This is disproved by the fact that no trace of either nitrite or nitrate has been found in bacteria or in their culture solutions.

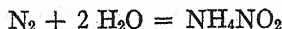
The reduction theory. This is supported by the occurrence of an increase, followed by a decrease, of ammonia in some culture solutions of Azotobacter.

Although the decrease of ammonia in culture solutions shows that nitrogen can be absorbed by bacteria in the form of ammonia, this does not prove that the nitrogen is fixed in the form of ammonia, since, for instance, the latter may have been produced from nitrite by reduction. It would, of course, be difficult to detect nitrite if its velocity of production from free nitrogen were slower than that of its transformation to ammonia.

Rossi (5) recently claimed, in accordance with Winogradsky's experimental findings (7), that the first process in nitrogen fixation by Azotobacter is the formation of ammonia. Winogradsky found that much ammonia was produced by Azotobacter in a silica-gel culture containing sodium lactate or succinate instead of mannite, as judged not only by chemical reaction but also by odor.

Wieland (6) explained the production of hydrazine in the fixation of nitrogen by Azotobacter on the basis of his theory of dehydrogenation. He assumed that a certain substance, which exists in bacteria and activates hydrogen, does not facilitate the combination of hydrogen with oxygen, but activates molecular nitrogen to form hydrazine. His experimental results proved the correctness of the oxidation process considered in his report but did not fully prove that of the mechanism of the nitrogen fixation.

A long time ago the senior author and his associates (1, p. 44; 2, p. 128; 4) suggested the formation of ammonium nitrite in nitrogen-fixing bacteria by the combination of one molecule of nitrogen with two molecules of water as follows:



This view was merely an opinion in regard to ammonia formation and was not proved experimentally.

Recently, Burk and Horner (3) reached the conclusion that the extracellular ammonia observed so far, in their own and in previous investigations, is in all probability derived entirely from the decomposition of normal cell nitrogen and not, in any measurable quantity, by direct synthesis from free N_2 by *Azotobacter*.

Since accurate analytical methods for the determination of nitrogen compounds produced in the bacterial cells or culture solutions are devised with difficulty, we made the following experiments in order to ascertain how the nitrogen in nitrate, nitrite, and ammonia would be utilized by *Azotobacter* when these compounds were added separately or in combination to culture solutions.

EXPERIMENTAL METHOD

Three strains of *Azotobacter* were used in our experiments, as follows: *Azotobacter chroococcum*, isolated from a field soil in China; *Azotobacter Beijerinckii*, isolated from the paddy field soil at the Shizuoka Agricultural Experiment Station; and *Azotobacter vinelandii*, isolated from the paddy field at the Miye Agricultural Experiment Station.

A slightly alkaline (pH 7.5) Ashby's culture solution containing the following compounds was used: mannite, 10.0 gm.; NaCl, 0.2 gm.; KH_2PO_4 , 0.5 gm.; CaSO_4 , 0.1 gm.; MgSO_4 , 0.2 gm.; distilled water 1000 cc. Molybdenum and iron were not specifically added, and all experiments reported were performed with inorganic nitrogen compounds, KNO_3 , NaNO_2 (or KNO_2), and $(\text{NH}_4)_2\text{SO}_4$, added at a concentration of 0.02–0.03 per cent, which is recognized as favorable for the growth of these bacteria.

The fixation of nitrogen by *Azotobacter* was not observed in such culture solutions containing fixed nitrogen, as table 1 shows. Duplicate 20-cc. portions of Ashby's culture solutions, containing the aforementioned inorganic nitrogen compounds respectively, were put into 100-cc. Erlenmeyer flasks, sterilized for 30 minutes for three successive days in Koch's apparatus, and then inoculated with a pure culture solution of *Azotobacter* and incubated at 28°–30°C. Each culture solution, after a given time, was diluted to 250 cc. with distilled water and was analyzed for nitrate, nitrite, or ammonia by the usual colorimetric methods (nitrate, with phenoldisulfonic acid; nitrite, with Gries reagents; and ammonia, with Nessler's reagent).

TABLE 1
*Nitrogen in culture solutions**

TIME	A. CHROOCOCCUM			A. VINELANDII		
	NO ₃ -N	NO ₂ -N	NH ₃ -N	NO ₃ -N	NO ₂ -N	NH ₃ -N
days	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
0	0.85	1.15	0.69	0.85	1.15	0.69
1	0.85	1.15	0.69	0.85	1.15	0.69
2	0.85	1.15	0.69	0.85	1.15	0.69
3	0.85	1.15	0.69	0.85	1.15	0.69
4	0.85	1.15	0.69	0.85	1.15	0.69
5	0.85	1.15	0.69	0.85	1.15	0.69
7	0.90	1.30	0.69	0.90	1.30	0.69
9	0.90	1.30	0.69	0.90	1.30	0.69
12	0.90	1.30	0.69	0.90	1.30	0.69

* 20 cc. of each culture solution was used, to which was added 0.83 mgm. NO₃-N, 1.22 mgm. NO₂-N, or 0.64 mgm. NH₃-N. Incubation at 28°-30°C.

TABLE 2
Production of NH₃-N from NO₃-N by Azotobacter

TIME	A. CHROOCOCCUM*					A. BEIJERINCKII†				A. VINELANDII†			
	NO ₃ -N disappeared		NO ₂ -N produced	NH ₃ -N produced		NO ₃ -N disappeared		NO ₂ -N produced	NH ₃ -N produced	NO ₃ -N disappeared		NO ₂ -N produced	NH ₃ -N produced
	per cent	mgm.	mgm.	mgm.	per cent	mgm.	mgm.	mgm.	mgm.	per cent	mgm.	mgm.	mgm.
0	0	0	0	0	0	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0
1	22	0.12	0.0020	0.01	4	0.03	0.0043	0.02	0.02	1	0.01	0.0078	0.02
	15	0.09	0.0016	3	0.03	0.0045	0.02	0.02	2	0.02	0.0072
2	31	0.18	0.0007	0.01	10	0.08	0.0018	0.03	0.03	12	0.10	0.0020	0.03
	39	0.17	0.0008	0.02	9	0.08	0.0018	0.03	0.03	18	0.15	0.0020	0.03
3	43	0.26	0.0008	0.03	0.0008	0.04	0.04	20	0.17	0.0010	0.03
	37	0.23	0.0008	0.03	0.0008	0.05	0.05	0.0008	0.03
4	45	0.27	0.0005	0.04	25	0.21	0.0007	0.04	0.04	25	0.21	0.0007	0.04
	40	0.24	0.0005	0.04	32	0.27	0.0007	0.04	0.04	22	0.19	0.0005	0.04
5	50	0.30	0.0003	0.03	29	0.24	0.0005	0.06	0.06	23	0.19	0.0007	0.04
	53	0.32	0.0003	0.04	38	0.31	0.0005	0.06	0.06	32	0.27	0.0007	0.04
7	61	0.36	0.0003	0.06	42	0.35	0.0003	0.06	0.06	35	0.29	0.0003	0.05
	60	0.36	0.0003	0.07	45	0.37	0.0003	0.06	0.06	37	0.31	0.0003	0.05
9	69	0.41	0.0003	0.05	0.0002	0.10	0.10	35	0.29	0.0001	0.04
	76	0.45	0.0003	0.06	0.0002	0.10	0.10	35	0.29	0.0001	0.04
12	76	0.45	0.08	59	0.49	40	0.33
	78	0.46	0.09	55	0.46

* 15 cc. of culture solution containing 4.3 mgm. KNO₃ (0.594 mgm. NO₃-N) was used.

† 20 cc. of culture solution containing 6 mgm. KNO₃ (0.832 mgm. NO₃-N) was used.

EXPERIMENTAL RESULTS

Change of N when each inorganic nitrogen compound is present separately in the culture solution. It is clear from table 2 and from figures 1, 2, and 3, that almost all the $\text{NO}_2\text{-N}$ disappeared after 5-6 days, $\text{NH}_3\text{-N}$ after 8-9 days, and $\text{NO}_3\text{-N}$ still more slowly. In culture solutions containing $\text{NO}_2\text{-N}$ much $\text{NH}_3\text{-N}$ was produced, reaching a maximum when all the $\text{NO}_2\text{-N}$ had disappeared; after this $\text{NH}_3\text{-N}$ disappeared very rapidly. Where $\text{NO}_3\text{-N}$ was added, its disappearance was relatively slow, 20 per cent still remaining after 12 days; and the production of $\text{NH}_3\text{-N}$ was very small. A small quantity of $\text{NO}_2\text{-N}$ was found in these culture solutions (table 2).

From the foregoing results, it may be deduced that the *Azotobacter* absorb $\text{NH}_3\text{-N}$ as their nutrient, and use $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ after reducing these to ammonia. The accumulation of $\text{NH}_3\text{-N}$ in the $\text{NO}_2\text{-N}$ solution indicates

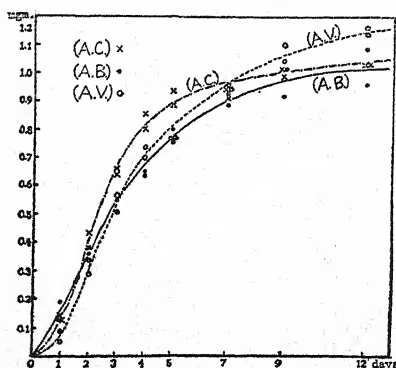


FIG. 1. ABSORPTION OF $\text{NH}_3\text{-N}$ BY AZOTOBACTER

A.C., A.B., and A.V. = *Azotobacter chroococcum*, *A. Beijerinckii*, and *A. vinelandii*, respectively. Culture solution used: 20 cc. containing 6 mgm. $(\text{NH}_4)_2\text{SO}_4$ (1.27 mgm. $\text{NH}_3\text{-N}$).

that the reduction velocity of $\text{NO}_2\text{-N}$ to $\text{NH}_3\text{-N}$ is more rapid than the velocity of absorption of $\text{NH}_3\text{-N}$ (fig. 2). The reduction velocity of $\text{NO}_3\text{-N}$ to $\text{NO}_2\text{-N}$ is apparently much slower than that of $\text{NO}_2\text{-N}$ to $\text{NH}_3\text{-N}$, since only a trace of $\text{NO}_2\text{-N}$ was detected in the $\text{NO}_3\text{-N}$ solution.

Change of N when two forms of inorganic nitrogen are present in the culture solutions. Figure 4 shows that *Azotobacter* absorb $\text{NH}_3\text{-N}$ after reducing $\text{NO}_2\text{-N}$, even in the presence of much $\text{NH}_3\text{-N}$ as NH_4NO_2 .

Figures 1 and 5 show that when equal quantities of $\text{NH}_3\text{-N}$ are added in the form of sulfate and nitrate, $\text{NH}_3\text{-N}$ disappears somewhat more rapidly in the former case than in the latter. This result was apparently due not to the direct influences of the SO_4 and the NO_3 ions, but to the consumption of $\text{NO}_3\text{-N}$ (presumably via reduction to $\text{NH}_3\text{-N}$). In this connection, table 3 shows that the sum of $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ of NH_4NO_3 disappeared is

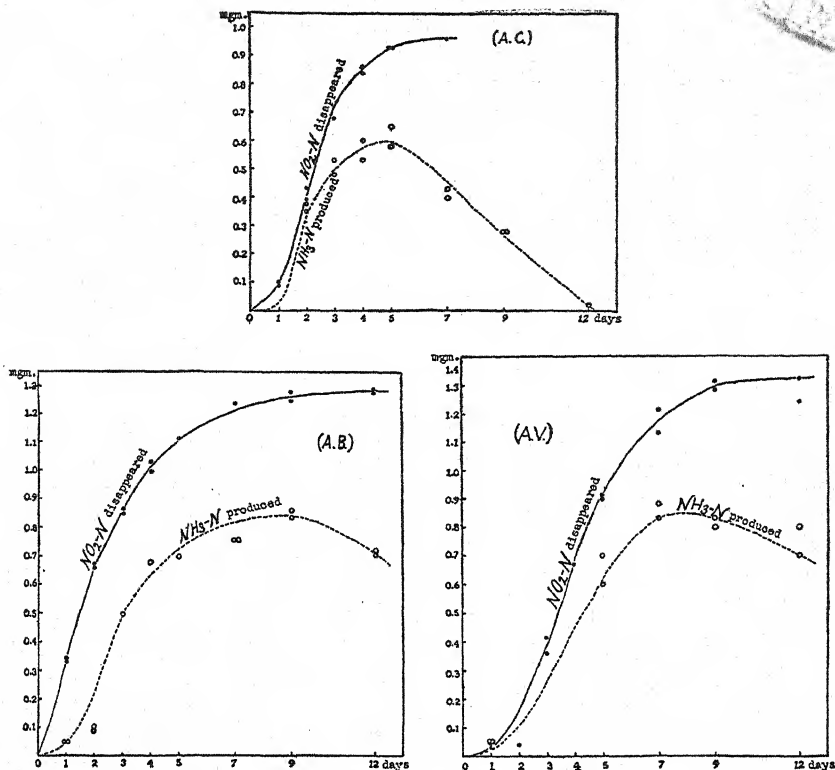


FIG. 2. PRODUCTION OF $\text{NH}_3\text{-N}$ FROM $\text{NO}_2\text{-N}$ BY AZOTOBACTER

A.C., A.B., and A.V. = *Azotobacter chroococcum*, *A. Beijerinckii*, and *A. vinelandii*, respectively. Culture solutions used: 20 cc. containing 8 mgm. KNO_2 (1.32 mgm. $\text{NO}_2\text{-N}$) with A.B. and A.V.; 15 cc. containing 5.81 mgm. KNO_2 (0.96 mgm. $\text{NO}_2\text{-N}$) with A.C.

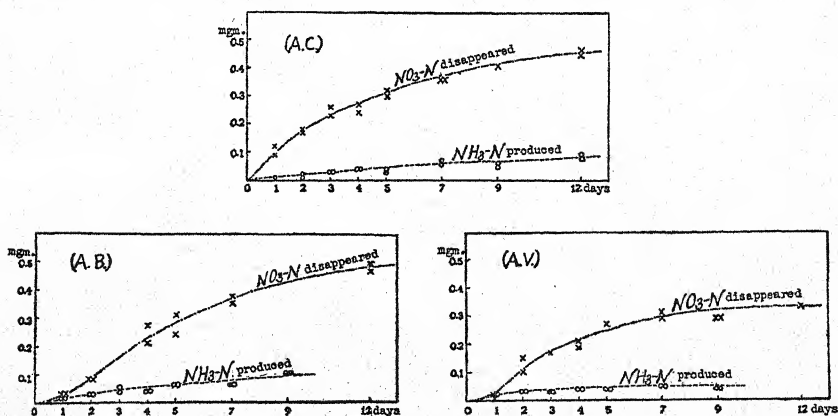
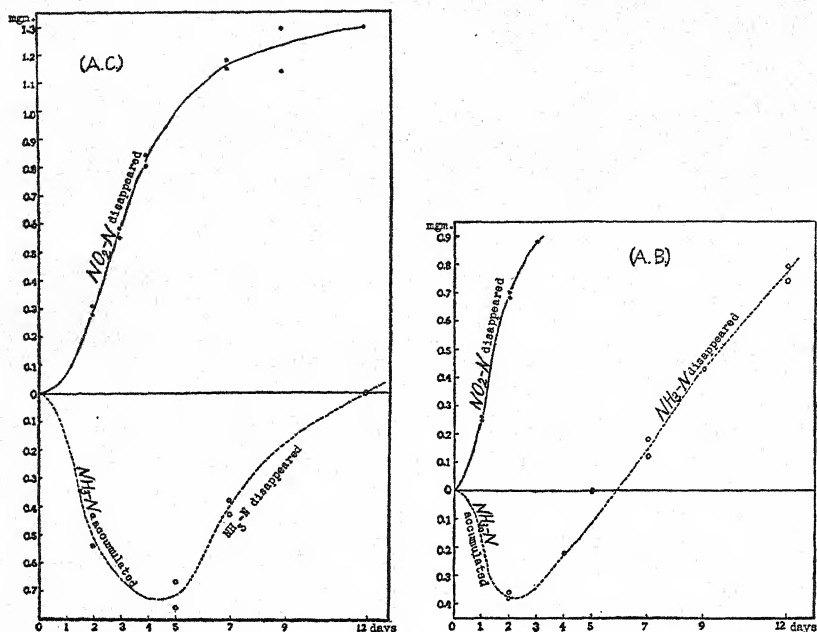


FIG. 3. PRODUCTION OF $\text{NH}_3\text{-N}$ FROM $\text{NO}_2\text{-N}$ BY AZOTOBACTER

A.C., A.B., and A.V. = *Azotobacter chroococcum*, *A. Beijerinckii*, and *A. vinelandii*, respectively. Culture solutions used: 15 cc. containing 4.3 mgm. KNO_3 (0.594 mgm. $\text{NO}_3\text{-N}$) with A.C.; 20 cc. containing 6 mgm. KNO_3 (0.832 mgm. $\text{NO}_3\text{-N}$) with A.B. and A.V.

FIG. 4. SELECTIVE ABSORPTION OF $\text{NO}_2\text{-N}$ AND $\text{NH}_3\text{-N}$ BY AZOTOBACTER

A.C. and A.B. = *Azotobacter chroococcum* and *A. Beijerinckii*, respectively. Culture solutions used: 20 cc. containing 6.46 mgm. NaNO_2 and 6.18 mgm. $(\text{NH}_4)_2\text{SO}_4$ (1.3 mgm. $\text{NH}_3\text{-N}$ and 1.3 mgm. $\text{NO}_2\text{-N}$) with A.C.; 20 cc. containing 4.32 mgm. NaNO_2 and 4.12 mgm. $(\text{NH}_4)_2\text{SO}_4$ (0.88 mgm. $\text{NH}_3\text{-N}$ and 0.88 mgm. $\text{NO}_2\text{-N}$) with A.B.

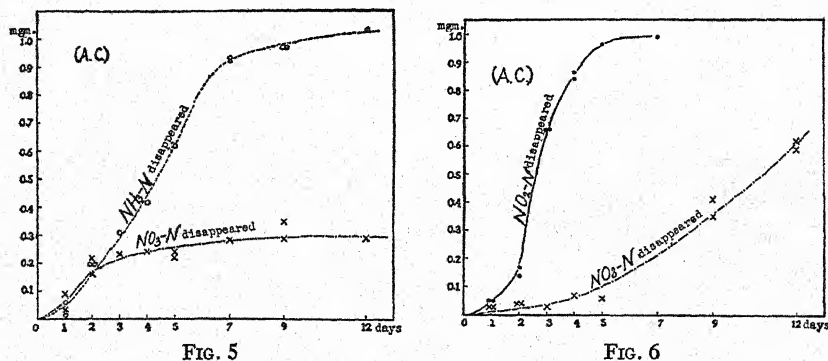


FIG. 5

FIG. 6

FIG. 5. SELECTIVE ABSORPTION OF $\text{NH}_3\text{-N}$ AND $\text{NO}_2\text{-N}$ BY AZOTOBACTER CHROOCOCCUM

Culture solution used: 20 cc. containing 6 mgm. NH_4NO_3 (1.05 mgm. $\text{NH}_3\text{-N}$ and 1.05 mgm. $\text{NO}_2\text{-N}$).

FIG. 6. SELECTIVE ABSORPTION OF $\text{NO}_2\text{-N}$ AND $\text{NO}_3\text{-N}$ BY AZOTOBACTER CHROOCOCCUM

Culture solution used: 20 cc. containing 6 mgm. KNO_2 and 6 mgm. KNO_3 (0.99 mgm. $\text{NO}_2\text{-N}$ and 0.83 mgm. $\text{NO}_3\text{-N}$).

almost equal to the quantity of $\text{NH}_3\text{—N}$ of $(\text{NH}_4)_2\text{SO}_4$ disappeared.¹ Furthermore, figure 6 shows that when equal quantities of KNO_2 and KNO_3 are added to culture solutions, the $\text{NO}_2\text{—N}$ disappears much more rapidly than does the $\text{NO}_3\text{—N}$.

The production of hydroxylamine by Azotobacter. By obtaining oxime-N in culture solutions to which NaNO_2 and a small quantity of acetone were added, we have succeeded in demonstrating the production of hydroxylamine as an intermediate product in the reduction of nitrite to ammonia by *Azotobacter*. The experiment was carried out as follows: 200-cc. portions of Ashby's culture solution containing 0.005 per cent of NaNO_2 were put into 500-cc. Erlenmeyer flasks, sterilized in the usual manner, and inoculated with three strains of *Azotobacter*. To these solutions acetone was added (1,000 cc.: 1 cc.), and the flasks were kept at 30°C . From time to time, parts of the culture solutions were taken and tested for nitrite. After all the $\text{NO}_2\text{—N}$ had disappeared, 2 gm. of CaCO_3 was added to each of the solutions, which was

TABLE 3
Absorption of nitrogen from $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 by Azotobacter chroococcum

TIME	$(\text{NH}_4)_2\text{SO}_4$	NH_4NO_3		
	$\text{NH}_3\text{—N}$ disappeared	$\text{NH}_3\text{—N}$ disappeared	$\text{NO}_3\text{—N}$ disappeared	Total N disappeared
days	mgm.	mgm.	mgm.	mgm.
1	0.13	0.05	0.05	0.10
2	0.40	0.18	0.12	0.30
3	0.65	0.30	0.19	0.49
4	0.80	0.45	0.23	0.68
5	0.90	0.62	0.26	0.88

then distilled. The distillate was collected in a flask containing 10 cc. of 0.1 *N* HCl , boiled to decompose the oxime (quite possibly acetoxime), neutralized, and tested with the following reagents:

1. 0.5 gm. of sulfanilic acid was dissolved in 150 cc. dilute acetic acid.
2. 0.1 gm. of α -naphthylamine was dissolved in 20 cc. water, and the colorless liquid was mixed with 150 cc. dilute acetic acid.
3. 1.3 gm. iodine was dissolved in 100 cc. of glacial acetic acid.
4. 0.5 per cent of sodium thiosulfate solution.

To the neutralized liquid, 2 cc. of reagent 1 and three drops of reagent 3 were added and shaken from time to time. After 5 minutes, the excess of iodine was removed with reagent 4, and 1 cc. of reagent 2 was added and left for a few minutes. If hydroxylamine is present in the solution, a red color appears.

¹ The quantity of total N which disappeared in the case of NH_4NO_3 is a little smaller than that in the case of $(\text{NH}_4)_2\text{SO}_4$, probably because of the slower velocity of disappearance of $\text{NO}_3\text{—N}$ compared to consumption of $\text{NH}_3\text{—N}$.

We have found that the three strains of *Azotobacter* used in this experiment produce hydroxylamine in culture solutions containing acetone, but the reaction was obtained only in traces when no acetone was present. We may conclude that hydroxylamine does not accumulate in culture solutions but is consumed (presumably via reduction to ammonia) immediately upon its production.

It is very interesting to observe that the toxic hydroxylamine is produced as an intermediate product in nitrite reduction by *Azotobacter* similarly to formaldehyde, which is believed by many to be produced as an intermediate product of the carbon assimilation by green plants.

SUMMARY

The decrease of $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NO}_3\text{-N}$, added separately or in combination to solution cultures of three species of *Azotobacter*, has been determined. Ashby's solution was employed, without specific additions of iron or molybdenum, and no experiments are reported in which fixation of nitrogen occurred in such culture solutions containing fixed nitrogen.

The velocity of consumption of $\text{NO}_2\text{-N}$ was the greatest; that of $\text{NO}_3\text{-N}$, the least.

In culture solutions containing nitrite, $\text{NO}_2\text{-N}$ disappeared very rapidly, and $\text{NH}_3\text{-N}$ accumulated, but this also disappeared rapidly after the complete disappearance of the nitrite.

When nitrate was added to culture solutions, a trace of nitrite and an accumulation of ammonia were found in the solution.

In culture solutions containing ammonium nitrite, the nitrite was for the most part first reduced to ammonia, even in the presence of added $\text{NH}_3\text{-N}$, and then absorbed by the bacteria.

From the aforementioned results, it is concluded that *Azotobacter* absorb nitrite, and possibly nitrate, mainly after reduction to ammonia.

Hydroxylamine is formed during reduction of nitrite to ammonia.

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CONTACT DEPLETION OF BARLEY ROOTS AS REVEALED BY RADIOACTIVE INDICATORS

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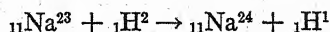
In a previous paper (2) we presented evidence for the existence of *contact effects* between plant roots and soil colloids. Whenever colloidal clay particles touch root surfaces, cations are transferred from the plant to the soil colloids. As a tentative theory we have assumed that such contact phenomena are the result of ion exchange between interpenetrating electric double layers, or more specifically, between overlapping oscillation spaces of adsorbed ions.

The recent discovery of artificial radioactivity provides a very sensitive and exceedingly simple method of chemical analysis. Moreover, the use of radioactive isotopes offers new perspectives for the study of ionic behavior in colloidal systems, in general, and in plants and soils, in particular. The present paper is an account of contact effect experiments conducted with radioactive sodium, potassium, and bromine. Again, the studies are concerned with contact depletion only; that is, transfer of nutrient ions from the root system to colloidal clay suspensions.

PRINCIPLES OF RADIOACTIVE INDICATORS

The cyclotron invented by O. E. Lawrence at the University of California is the most efficient tool for the creation of radioactive isotopes. The cyclotron produces high-speed protons and deuterons. Atomic nuclei, when subjected to bombardment by protons and deuterons undergo transformations which result in the production of radioactive isotopes. Physicists have been able to induce radioactivity in most of the elements of the periodic table. This achievement is opening new possibilities for research on many problems of biology and agriculture.

Transformation processes of atomic nuclei are expressed in the form of equations as shown in the following example:



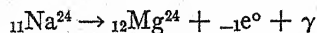
The equation indicates that ordinary sodium with atomic number 11 and

¹ The authors are indebted to D. R. Hoagland for valuable discussions and suggestions, and to E. O. Lawrence, director of the Radiation Laboratory, for supplying radioactive elements.

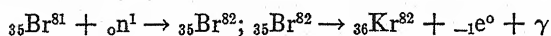
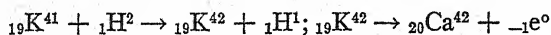
² Division of Plant Nutrition, College of Agriculture.

atomic weight 23 is bombarded by deuterons (${}_1\text{H}^2$) of atomic number 1 and atomic weight 2. Deuterons are heavy hydrogen nuclei each of which consists of one proton (${}_1\text{H}^1$) and one neutron (${}_0\text{n}^1$). When deuterons strike Na with sufficiently high velocity the neutrons combine with Na and form an isotope (${}_{11}\text{Na}^{24}$), that is, sodium with atomic number 11 but atomic weight 24. The protons (${}_1\text{H}^1$) escape.

This artificially produced isotope of sodium is radioactive and disintegrates with a half-life period of 14.8 hours into magnesium (${}_{12}\text{Mg}^{24}$), giving off beta radiations (β' or ${}_{-1}\text{e}^0$) and gamma radiations (γ). The disintegration equation reads as follows:



The corresponding equations for potassium and bromine are as follows:



From the standpoint of biological research one of the most significant characteristics of radioactive isotopes is their chemical behavior. Radioactive potassium, for instance, acts chemically like ordinary potassium. The two types of atoms cannot be separated by chemical means, since it is only the atomic nuclei which have different properties. The electron configurations, upon which the chemical behavior of the elements depends, are identical in both cases. Consequently, if a solution of KCl containing both ordinary and radioactive K—the latter in minute amounts—is used as a nutrient medium for plants, the roots should not be able to distinguish between the two kinds of ions and should accumulate both of them in their respective proportions. This, barley plants actually do, as will be shown elsewhere. Inasmuch as the radioactive members of the K ions continuously emanate β radiation, which may be easily detected with a Geiger counter, it is possible to trace the fate of the radioactive K within the plant in great detail. In this manner the radioactive isotopes serve as tags or indicators of ordinary elements.

METHODS OF EXPERIMENTATION WITH PLANTS

All tests were conducted with barley plants. These were grown according to the method of Hoagland and Broyer (1), as described previously (2). When the plants were about 3 weeks old, their roots were immersed in a solution containing radioactive elements. The migration of the radioactive isotopes into the shoots could be readily traced with the aid of the Geiger counter. By this means it was found that within 2 to 5 hours the plants accumulated substantial amounts of the radioactive elements.

The roots were then rinsed in flowing distilled water for about one minute, and subsequently were transferred to the test solutions. All experiments were

carried out with entire plants. The plants were grown from seedlings which had been fixed in the holes of supporting corks with nonabsorbent cotton. In most of the treatments reported here, the corks containing the plants were set in place in Mason jars to which had been added the desired solutions and suspensions. In all cases there were seven plants in one cork. In later discussions the expression, "one cork" will refer to the seven plants contained in one cork. The outgo of radioactive elements from the roots to the surrounding medium was ascertained by analysis of the nutrient solution for radioactivity.

Geiger counter

The activities of the samples were determined by the use of the Geiger-Müller or wire-and-cylinder type counting tube. The instrument was provided with a thin glass window to permit greater penetration of beta rays. The tube was filled with hydrogen gas at 10 cm. pressure. The cylinder was made of copper; and the central wire, of tungsten. As the behavior of the Geiger-Müller counter has been adequately described by Werner (3, 4), the following brief description of its action is sufficient: The tube is connected in series with a high resistance (5×10^8 ohms) and a high voltage (1200 volts). A beta ray or gamma ray on entering the tube initiates a corona discharge between the wire and cylinder by ionization of the H_2 gas. The corona current, i , in the high resistance, R , produces an iR potential drop which lowers the potential below the corona threshold, and the corona extinguishes. The iR drop of the instantaneous current can be amplified and counted by means of a suitable counting circuit. The instrument used in this research was provided with a Neher type amplifying circuit which operated a mechanical recorder. Since cosmic rays and other factors which are always present also cause discharges in the tube at a more or less constant rate, all counts of radioactive materials must be corrected for this so-called "background" count. Thus each count above the background corresponds to the disintegration of a single radioactive atom. The fraction counted of the total number of disintegrations of the sample depends, however, on the fraction of the total number of emitted beta or gamma rays which enter the tube.

Method of counting

The number of counts per minute obtained from a radioactive sample greatly depends on how close the substance is brought to the surface of the counter tube.

In the case of solutions which were strongly radioactive and emitted the penetrating gamma radiation (sodium and bromide), the counter tube, shielded by a pyrex centrifuging glass, was dipped directly into the liquid (400 cc.).

Radioactive K systems were measured in a different manner. An aliquot of 25 cc. was evaporated to dryness, and the residue was transferred to a watch glass and then held directly under the counter tube. Whenever salt solutions

had to be compared with clay suspensions, enough nonradioactive clay was added to the solution aliquots to guarantee strictly comparable conditions of counting.

All activities are expressed in "counts per minute." The variability of the atomic disintegrations calls for statistical treatment of the results. As a rule, we have made ten 1-minute readings with the counter and have calculated the mean error (M) of the mean according to the equation:

$$M = \sqrt{\frac{\sum d^2}{n(n-1)}},$$

where d denotes the difference of an observation from the arithmetical average and n indicates the number of observations.

At times the individual 1-minute readings were omitted, and only the sum total of the counts for a period of 5 to 10 minutes was recorded. Under such circumstances the mean error (M) was calculated from the equation:

$$M = \frac{\sqrt{c}}{m},$$

where c indicates the sum total of the counts obtained during the period of m minutes. As an illustration, the following data were obtained on 25 cc. of radioactive Mg-K-clay suspension. Counts per minute: 107, 81, 78, 106, 105, 83, 93, 102, 107, 105; average = 96.7 ± 3.83 .

All errors reported in this paper refer to the error of counting as calculated from the foregoing equations. These values do not contain the variability of the corks (seven plants per cork) or the variations due to different treatments. The "over-all" error was determined in a special experiment involving 24 corks (seven plants each) and four widely different treatments consisting of six replications each. This error, calculated from the equation:

$$M_c = \sqrt{\frac{\sum d^2}{n-1}} \quad (n = 24)$$

was 9.9 per cent, for one cork, whereas the counting error of this series amounted to only 1 to 3 per cent per cork. Depending on the accuracy of the counts, the errors listed in this paper exceed or fall below the over-all error. Consequently, if one wishes to test the significance of the difference of two types of treatments the mean error (or standard error) of one cork, which is 9.9 per cent, must be taken into consideration.

Background

In the present research the value of the background count varied between 15 and 30 counts per minute, depending on the locality (greenhouse or dark room inside a concrete building). The variability is indicated by the following typical series which comprises ten consecutive recordings of 1-minute duration

each. Counts: 19, 24, 22, 19, 16, 20, 31, 29, 27, 17; average = 22.4 ± 1.51 counts per minute. The background was frequently measured.

All values for radioactivity were corrected for the background. The data obtained for Mg-K-clay may serve as an illustration.

Counts for Mg-K-clay.....	96.7 \pm 3.83
Background.....	25.3 \pm 1.69
Difference.....	71.4 \pm 4.18

The value of 71.4 ± 4.18 counts per minute represents the radioactivity of 25 cc. of Mg-K-clay suspension, measured by the dry technic. The mean error of the difference (M_d) follows from the equation:

$$M_d = \sqrt{M_1^2 + M_2^2},$$

where M_1 and M_2 denote the mean errors of the two observations.

Correction for radioactive decay

When a radioactive substance is allowed to remain in the vicinity of a Geiger counter, it is found that the number of counts per minute decreases as a function of time. The decrease is governed by the relationship:

$$I = I_0 e^{-kt}$$

where I represents the intensity of radioactivity (e.g., counts per minute) at the time t and I_0 , the initial intensity; k is a constant, characteristic of each radioactive element. In practice it is customary to express the rate of decay in terms of the half-life period; that is, the time interval during which the substance loses 50 per cent of its radioactivity. For potassium the value is 12.4 hours. The following equations hold for radioactive K:

$$\frac{I}{I_0} = \frac{1}{2} = e^{-k \cdot 12.4},$$

k becomes 0.0559, and

$$\frac{I}{I_0} = e^{-0.0559t}$$

Measurements obtained with the Geiger counter refer to I . To enable comparison of different observations, the counts must be expressed as I_0 . All values for radioactivity reported in this paper refer to I_0 . The mode of calculation is seen from the following example. Plants containing radioactive K were transferred to a Mg-clay suspension on July 5, at 4:52 p. m. After 3.80 hours (at 8:40 p. m.) 25 cc. of clay suspension was removed from the jar. Actual counting did not occur until 11:36 p. m. The counts, corrected for background, amounted then to 71.4 ± 4.18 per minute, as shown in the pre-

ceding section. This value must be corrected for the time elapsed. The time $t = 0$ was arbitrarily selected for all measurements on July 5 as 4:00 p. m. The time interval is, therefore, 7.60 hours, and the equation assumes the form:

$$I_0 = \frac{I}{e^{-0.0559 \times 7.60}}, \text{ or } I_0 = 1.53I$$

The value of counts, corrected for radioactive decay, is therefore 109 ± 6.4 . This represents the corrected radioactivity of 25 cc. of the Mg-K-clay suspension which had been in contact with plant roots for a period of 3.80 hours.

EXPERIMENTS WITH RADIOACTIVE POTASSIUM

All samples of radioactive potassium were prepared by bombarding metallic K with high-speed deuterons. To remove possible impurities (Na, Cu, Zn) the radioactive K was repeatedly recrystallized as potassium tartrate. The element was supplied to the plants in the form of potassium nitrate.

Behavior of radioactive K plants in distilled water

On June 3, 1938, the roots of seven plants which had accumulated radioactive K were immersed in 900 cc. of distilled water. This set was replicated three times. In a corresponding series 0.44 m.e. of CaCl_2 was added to provide a more suitable physiological solution. Tests for radioactivity of the water were run on 25-cc. aliquots after contact periods of 2.6, 10.8, and 55 hours. The average counts per minute above background are assembled in table 1. Some values are positive and some are negative, indicating that no significant outgo of K occurred. Moreover, the magnitudes are within the variability of the background, the mean error of which is ± 1.62 . The initial pH of water was 5.8; at the end of the experiment the pH was 4.8.

A second experiment was conducted on July 4. Aliquots of 25 cc. were drawn after immersion periods of 3.72 hours and 6.53 hours. The counts per minute above background were as follows:

$$\text{H}_2\text{O (3.72-hour period)} = 8.1 \pm 3.82$$

$$\text{H}_2\text{O (6.53-hour period)} = 6.6 \pm 5.36$$

Although both values are positive, their magnitudes are not highly significant. As the roots themselves gave 77,000 counts per minute, the loss of radioactive K, if any, must have been very small.

In summarizing, we may conclude that the barley plants under consideration possess a pronounced tendency to retain radioactive potassium against distilled water. These findings fully corroborate the results of our previous experiments in which excised barley roots did not lose measurable amounts of K to distilled water during 10 hours.

Behavior of radioactive K plants in electrolyte solutions

Plants containing radioactive K were placed in 900 cc. of various chloride solutions containing 5 m.e. of cation per liter and, in each case, 0.5 m.e. CaCl_2

per liter (June 3). After 11 hours the roots had rendered some of the solutions radioactive, as indicated in table 2. The counts for H_2O , LiCl , and NaCl were within the variability of the background and are therefore listed as "none." The values for MgCl_2 , CaCl_2 , SrCl_2 , and BaCl_2 likewise did not exceed the background. A corresponding series with K salts (3 m.e. per liter) showed that the inorganic anions which are common to nutrient solution exerted no specific influence on the release of radioactive K from roots. As to the total amounts of K transferred, no accurate information can be given. The original KNO_3 solutions which contained radioactive K and into which the plants were placed for K absorption contained 0.000213 m.e. of total K per 100 counts per 25 cc. Since the ratio $\frac{\text{total K}}{\text{radioactive K}}$ is higher inside the plant than outside,

TABLE 1
Outgo of radioactive K into water

SYSTEM	COUNTS PER MINUTE PER 25 CC.		
	After 2.6 hours	After 10.8 hours	After 55 hours
Plants in distilled water.....	+0.6	-3.1	± 0
Plants in $\text{H}_2\text{O} + \text{CaCl}_2$	+0.7	-0.3	+3.6

TABLE 2
Outgo of radioactive K from roots into electrolyte solutions
(Counts per minute, above background)

SOLUTION	FINAL pH	COUNTS PER MINUTE PER 25 CC.	SOLUTION	FINAL pH	COUNTS PER MINUTE PER 25 CC.
H_2O	5.80	None	KCl	4.50	42.8 ± 9.8
LiCl	5.75	None	KNO_3	6.05	47.2 ± 9.5
NaCl	5.20	None	K_2SO_4	3.85	40.4 ± 9.8
KCl	4.40	62.5 ± 10.5	KH_2PO_4	4.10	47.1 ± 10.8
HCl	2.45	219 ± 11.8	KHCO_3	6.70	35.7 ± 10.7

we may only infer that *at least* 0.000213 m.e. of K per 100 counts per 25 cc. must have left the roots.

In conclusion it may be said that the barley roots have a tendency to yield measurable amounts of K to certain electrolyte solutions. No such losses were observed in our previous experiments. Probably the great sensitivity of the radioactive method accounts for the discrepancy. It is probable, however, that the losses in the case of the rather strong HCl (0.005 *N*) solution are due to injury.

Behavior of radioactive K plants in clay suspensions

The clays used in the present study are bentonites and Yolo clay colloids. Both consist of the common clay mineral montmorillonite. The base-saturated

bentonites were prepared by adding hydroxides to electrodyalyzed colloids. Their base-exchange capacity as determined with neutral ammonium acetate is 100 m.e. per 100 gm. oven-dry material. The base-saturated Yolo colloids were obtained by extensive leaching with neutral salts. The base-exchange capacity of these clays is 55 m.e. per 100 gm.

Corks holding seven radioactive plants were transferred, on June 3, 1938, to clay suspensions and salt solutions of 900 cc. volume each. All jars contained 4.5 m.e. of total cations and, in addition, 0.45 m.e. CaCl_2 . After a contact period of 53 hours the counts listed in table 3 were obtained from the solutions and suspensions. In all cases the K- and Na-clay sols give higher counts than do the corresponding K and Na chlorides. In other words, the plant

TABLE 3

Outgo of radioactive K from roots into clay suspensions and chloride solutions (53 hours)

SOLUTIONS	COUNTS PER MINUTE PER 25 CC.	CLAY SOLS	COUNTS PER MINUTE PER 25 CC.
H_2O	None	H_2O	None
NaCl	None	Na-Yolo clay	606 \pm 93
KCl	314 \pm 69	K-Yolo clay	374 \pm 60

TABLE 4

Outgo of radioactive K from roots into chloride solutions and clay suspensions containing divalent cations

SALT SOLUTIONS			CLAY SUSPENSIONS (1 PER CENT)		
Type	Initial pH	Counts per minute per 25 cc.	Type	Initial pH	Counts per minute per 25 cc.
MgCl_2	6.35	3.3 \pm 4.1	Mg-Yolo	7.20	109 \pm 6.4
CaCl_2	6.00	11.3 \pm 3.7	Ca-Yolo	7.25	66.3 \pm 3.8
CaCO_3	9.45	17.0 \pm 4.1			
SrCl_2	6.10	13.5 \pm 4.6	Sr-Yolo	6.75	68.4 \pm 6.3
BaCl_2	6.10	2.8 \pm 3.5	Ba-Yolo	6.85	45.2 \pm 4.8

roots lost more K to the clay suspensions than to the true solutions. This feature is particularly pronounced for the Na-systems. For the K-systems the difference does not exceed the limits of variability.

Further confirmation was obtained on July 4, when the roots were kept for 3.7 hours in 400-cc. Mason jars. Table 4 shows the results obtained with divalent cations for concentrations amounting to 5.5 m.e. per liter. The data convincingly prove the great superiority of the clay sols in extracting radioactive K from barley plants. The value for Mg-Yolo clay is highest among the di-clays.

At the same time a strict comparison was made between monovalent and divalent cations. This was carried out in the form of a concentration series which comprised the systems KCl , CaCl_2 , K-Yolo clay, and Ca-Yolo clay.

The amounts of cations contained in 400 cc. were 0.67, 2.2, 11.0, and 22.0 m.e. The counts per minute per 25 cc. are graphically illustrated in figure 1. Two features are outstanding: first, the systems with monovalent cations, whether chlorides or clay sols, caused the loss of more radioactive elements from the roots than did the media containing divalent cations; second, the clay systems, irrespective of the valence of the adsorbed cations, gained more radioactivity than the true solutions.

In general, the observations with radioactive K fully confirm our previous results on the influence of colloidal particles on the ion distribution between plant roots and clay media. New is the observation that divalent cations, if

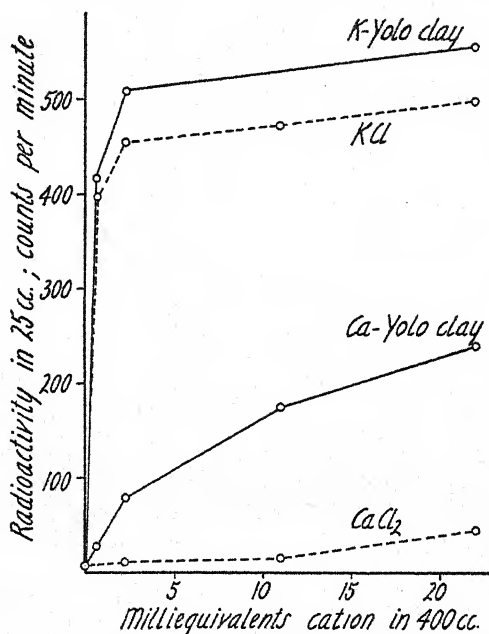


FIG. 1. OUTGO OF RADIOACTIVE POTASSIUM FROM ROOTS INTO CLAY SUSPENSIONS AND SALT SOLUTIONS

adsorbed on clays, also reduce the K level of the barley plants used in these investigations.

EXPERIMENTS WITH RADIOACTIVE SODIUM

Metallic sodium, after treatment with high-speed deuterons, was dissolved in water, filtered to remove insoluble hydroxides and carbonates, and neutralized with HCl. On June 1, 1938, radioactive Na as NaCl (1.9 m.e. total Na) was added to the Hoagland solutions in the pans used for growing plants. The shoots became strongly radioactive, after an absorption period of 3 hours. After the roots had been rinsed with distilled water, the plants were transferred to pint Mason jars containing the desired salt solutions and clay suspensions.

The media were tested for radioactivity after 3 hours and 16 hours. The counts per minute are presented in table 5. The outstanding difference between the radioactive Na and K plants is the significant loss of radioactive Na to distilled water. Whether this is characteristic for Na in general or merely a consequence of the Na status of the barley plants investigated is not known. In contrasting clays with solutions, it is seen that the sols tend to enhance the outgo of Na from the roots, especially after prolonged periods of contact. Strict comparison is not possible since the systems differ in their cation composition. This objection does not apply to the data in table 6 which shows the

TABLE 5
Outgo of radioactive Na from roots into true and colloidal solutions

SYSTEM	COUNTS PER MINUTE	
	After 3 hours	After 16 hours
H ₂ O.....	106 \pm 4.4	194 \pm 10
KCl (5 m.e./l.).....	108 \pm 7.5	316 \pm 17
CaCl ₂ (5 m.e./l.).....	106 \pm 7.3	52 \pm 8.6
Hoagland solution.....	101 \pm 7.1	247 \pm 15
H-Putnam clay.....	83 \pm 6.8	375 \pm 18
H-Cecil clay (0.5 per cent).....	96 \pm 7.1	357 \pm 18
H-Lindley clay.....	185 \pm 9.3	498 \pm 20
H-peat (2.2 per cent).....	309 \pm 12	603 \pm 22
H-bentonite (0.5 per cent).....	280 \pm 11	668 \pm 27

TABLE 6
Outgo of radioactive Na from roots into Na-systems

SYSTEM (5 M.E. Na PER LITER)	COUNTS PER MINUTE	
	After 3 hours	After 16 hours
H ₂ O.....	106 \pm 4.4	194 \pm 10
NaCl.....	102 \pm 7.2	229 \pm 14
NaHCO ₃	78 \pm 6.5	298 \pm 16
Na-bentonite.....	147 \pm 8.4	339 \pm 17

loss of radioactive Na to various Na solutions and Na-clay suspensions. Again the colloidal solutions acquire the highest amounts of radioactivity.

Briefly summarized, the findings with radioactive Na corroborate the observations made with K as far as the efficiency of root depletion by colloidal systems is concerned.

EXPERIMENTS WITH RADIOACTIVE BROMINE

For most clays the adsorption capacity for anions such as Cl, Br, NO₃, and SO₄ is very low. One would not anticipate therefore an enhanced withdrawal of Br from barley roots by clay particles.

If a flask containing ethyl bromide is placed in the path of neutron rays, radioactive Br_2 is formed. NaBr is obtained by shaking the ethyl bromide with a mixture of Na-sulfite and Na-bicarbonate solutions. Purification of the extract was carried out by steam distillation (140°C.), after addition of phosphoric acid. The resulting HBr was neutralized with KOH . Radioactive KBr thus produced was added to pans of solution to the extent of 0.35 m.e. of total Br per 168 plants (Sept. 22, 1938). After 5 hours the plants, seven per cork, were transferred to the salt and clay solutions where they remained from 4 to 9 hours. The radioactivity was tested on the total 400-cc. sample.

From the data in table 7 some very interesting conclusions may be drawn. As was anticipated, the clay colloids no longer exceed the chlorides in their ability to extract nutrient ions from plants. In all cases, the counts for the suspensions of negative particles are below those for the solutions. On the

TABLE 7
Outgo of radioactive Br from barley roots into salt solutions and clay sols

PURE SOLUTIONS	INITIAL pH	TIME	COUNTS PER MINUTE	COLLOIDAL SOLUTIONS	INITIAL pH	TIME	COUNTS PER MINUTE
		<i>hours</i>				<i>hours</i>	
H_2O	5.80	5.6	15.6 ± 2.1	Na-Yolo clay	7.50	8.5	19.6 ± 2.3
NaCl	5.80	8.6	27.5 ± 2.5	K-Yolo clay	7.00	6.3	17.4 ± 2.1
KCl	6.05	6.4	29.9 ± 2.4	Mg-Yolo clay	7.05	7.7	5.5 ± 1.9
MgCl_2	5.85	8.3	10.0 ± 3.7	Ca-Yolo clay	7.15	6.4	6.9 ± 1.9
CaCl_2	6.15	7.7	88.6 ± 3.5	H-Yolo clay	4.65	5.7	11.1 ± 1.9
KHCO_3	9.55	6.5	110.0 ± 3.8	Aiken soil	6.50	5.3	11.0 ± 1.9
KHCO_3	6.95*	17.8	24.3 ± 2.9	$\text{Fe}(\text{OH})_3$	5.5	37.2 ± 2.5

* Final pH.

other hand, the electrodialyzed iron hydroxide sol which contains no free electrolytes exceeds the water value by more than 100 per cent. These observations are in harmony with colloid chemical considerations, since the negative clay particles have no affinity for halogen anions whereas the positive iron hydroxide particles will adsorb bromides. Such findings forcefully bring to the fore the importance of soil colloids in influencing the ion status of root systems.

MEMBRANE EXPERIMENTS

Contact depletion of living roots by clay particles should not take place if the two colloidal systems are separated by a membrane which permits passage of small ions only. On November 4, at 9:00 p. m. radioactive K plants were placed in four pyrex trays containing 1200 cc. of distilled water which was aerated continuously. Into each vessel was dipped a pyrex flash which had a bottom consisting of a semipermeable membrane (Visking casing). At the

beginning of the experiment the following solutions, 50-cc. each, were introduced into the membrane flasks:

Flask 1: H_2O .

Flask 2: KCl (6.25 m.e.).

Flask 3: KHCO_3 (6.25 m.e.).

Flask 4: K-Yolo clay (6.25 m.e.).

After 12.3 hours, during which time the solutions and suspensions inside the membrane flask were constantly agitated with a stream of carbon dioxide, counts were taken of the entire 50 cc. of the solutions inside the membrane (the roots were outside the membrane). The counts above background were as follows:

H_2O	0.6 ± 1.97
KCl	16.1 ± 1.36
KHCO_3	49.1 ± 2.54
K-Yolo clay.....	6.8 ± 1.77

The result shows that in the presence of the membrane the clay solution was less effective than were the salt solutions, whereas in the absence of a membrane the contrary effect was observed, as indicated by all our previous experiments. In a parallel experiment run under identical conditions, but without a membrane, the following counts for 50-cc. solutions were obtained:

H_2O	2.5 ± 4.3
KCl	60.8 ± 5.9
KHCO_3	58.8 ± 6.1
K-Yolo clay.....	76.4 ± 5.8

In harmony with our previously reported data on excised roots in which it was shown that membranes prevent the withdrawal of K from excised barley roots by H-bentonite, it must be concluded that contact is a necessary requirement for the observed cation removal from roots by colloidal clay particles.

A NEW ASPECT OF IONIC INTERRELATION OF PLANT ROOTS AND NUTRIENT MEDIA

The use of radioactive isotopes has brought to light a process which no other technic could have revealed. As seen from figure 1 the KCl solutions and the K-clay suspensions show marked gains of radioactive potassium which has been given off by the roots. Now, we have good evidence to assert that the very same plants have accumulated substantial amounts of K from the media. One must conclude, therefore, that potassium migrated simultaneously in opposite directions, namely, into the root and out of the root. These relationships were examined quantitatively on June 3, 1938. Twelve corks each holding seven plants containing radioactive K were placed in a shallow tray of pyrex glass which contained 1800 cc. of K-Ca-bentonite suspension (0.35 per cent). The suspension, which was renewed five times at intervals of 1

hour, acquired a total activity corresponding to 53,640 counts per minute. As the radioactivity of the original KNO_3 solution was 1 count per 2.13×10^{-6} m.e. K, the 84 plants must have given off 0.114 m.e. K to the K-Ca-bentonite suspensions. This value represents a minimum amount only, for reasons already given. Prior to immersion in K-Ca-bentonite, the roots weighed 4.51 gm. (on an oven-dry basis) and contained 1.685 m.e. K; afterwards, the analysis showed 2.840 m.e., or a gain of 68.3 per cent. Actually the roots must have absorbed a larger amount of K, since at least 0.114 m.e. moved out of the plants. The accumulation of 1.155 m.e. K represents a net intake which may be considered as the consequence of ion interchange between radioactive and ordinary K of the plant and ordinary K of the solution.

Similar relationships exist for other cations. According to table 5, radioactive Na roots lose Na to Na-bentonite while at the same time they more than double their original Na level. Radioactive Br roots (table 7) transplanted in KBr give off 30.1 ± 1.98 counts per minute within 4.3 hours; yet they absorb large amounts of the electrolyte.

In view of the findings, our concepts of the mechanism of electrolyte absorption by plants must be modified and extended. The results show that the intake of ions is not a uni-directional process; ions of the same species may move into the root and out of the root at the same time. *The outgo is especially pronounced when the roots are in contact with colloidal systems.*

The outgo of ions through contact effects can occur with actively metabolizing root systems, capable of further salt absorption, but it is not yet possible to state the role of metabolism in the loss of mineral ions to colloids or to salt solutions, although certain experiments suggest that root metabolism associated with salt accumulation may have a relation to the exchange processes which bring about loss of ions from the root system. This question is under further investigation. At present, emphasis is placed on the general phenomenon of removal of ions from active roots, especially under conditions of root-colloid contacts. This, in itself, has an interesting and important bearing on certain problems of soil-plant interrelations, regardless of the nature of the physiological or chemical mechanisms of the root resulting in loss of ions.

THE PROBLEM OF ROOT INJURY

The foregoing experiments convincingly demonstrate the significance of ion interchange between roots and colloidal clay particles. Moreover, the trials with membranes strongly point toward the existence of a specific contact phenomenon which we interpret as an ion interchange between intermingling electric double layers. For obvious reasons, such a picture is purely theoretical, since all knowledge of the fine structure of root surfaces and the behavior of ions on surfaces in general is based on inferences. Indeed, one might contend that the entire effect is merely the result of injury of roots. One might suggest that in healthy roots the movement of an ion in process of accumulation is

uni-directional and that any loss of an ion of the same species constitutes definite proof of cell injury.

For the systems under consideration two main sources of root injury should be taken into consideration. One of them may be an unfavorable balance of electrolytes in the culture solution; the other, a direct effect of the colloidal particles such as physical rupture of cell walls or localized dehydration.

Regarding the pure electrolyte effect we note from preceding tables that the roots lose radioactive K to mixtures of salts containing Ca ions as well as to single salt solutions comprising monovalents cations. According to table 5, roots, within 3 hours, transfer radioactive sodium in equal amounts to H_2O , KCl, and Hoagland solution. In a special experiment in which roots of plants containing radioactive K were placed in flowing nutrient solution (full Hoagland solution), 23.7 per cent of the total radioactivity of the roots was removed in 48 hours.

Unless one maintains that nutrient solutions of the Hoagland type are toxic or injurious to roots, there is little justification for attributing the outgo of cations from roots to electrolyte injury. The other alternative, namely, the belief that the observed simultaneous transfer of ions from root to media, and vice versa, is a normal process of healthy roots, appears preferable.

In regard to direct contact injury the H- and K-colloids should be most harmful, since they deplete the roots more efficiently than other types of clay. One would expect that such disturbances of roots cells are accompanied by losses of *anions* as well as cations, a criterion which may be easily subjected to experimental verification. The results obtained with radioactive bromide anions (table 7) constitute sufficient proof that colloidal clays in general and H-clay in particular do not cause significant losses of Br. The counts for H-Yolo clay are even below those of distilled water. Thus if a plant contains sufficient amounts of KBr, a H-clay will pull out K but not Br, whereas a positive iron hydroxide sol removes Br, but not K, from the roots. Such behavior of roots does not speak in favor of the direct injury hypothesis.

The following test for injury is particularly illuminating:

Radioactive barley roots possessing an activity of 7330 counts per minute were placed into 400 cc. of distilled water, H-Yolo clay, and K-Yolo clay suspensions. After a contact period of 2.58 hours the solutions had acquired the following activities (counts per minute per 25 cc.):

H_2O	6.1 \pm 2.6
H-clay	132 \pm 4.4
K-clay	193 \pm 7.1

All plant roots were then washed for 1 minute and immediately transferred to distilled water for the purpose of learning whether or not the roots continued to give off large amounts of radioactive K. This should occur if the aforementioned losses of K were the result of root injury. Although the measurements were taken for short intervals, all systems gave very low counts (table 8),

for the technic employed in this study. Especially conclusive are the results of the K-clay systems in which the roots released 42 per cent of their radioactivity to the clay suspensions but, after transfer to distilled water, immediately reduced the outgo of K to such a low degree that no losses could be detected with the present method of counting. Any injury resulting from contact with clay particles must have been concomitant with the period of treatment, and it must have ceased at once thereafter. It is doubtful that "injury" is the appropriate term to describe such plant behavior.

GENERAL CONCLUSIONS

The investigations with radioactive isotopes fully confirm the contact depletion effects observed in previous studies with excised barley roots.

It is now fairly certain that the classical theories of soil solutions no longer suffice to explain fully the absorption of mineral elements by plants from soils. They must be supplemented by considerations of contact effects. Although contact intake has not yet been proved, the converse phenomenon, namely, contact depletion, is well established for the barley plants herein described.

TABLE 8

Injury test

SYSTEM	COUNTS PER MINUTE PER 25 CC.		
	After 15 minutes	After 1 hour	After 2.58 hours (extrapolation)
Water-roots into H ₂ O.....	2.3 \pm 6.5	5.7 \pm 6.7	12.5 \pm 19.4
H-clay-roots into H ₂ O.....	13.4 \pm 7.1	21.6 \pm 7.6	43.8 \pm 17.1
K-clay-roots into H ₂ O.....	10.5 \pm 7.0	8.0 \pm 7.1	3.1 \pm 2.3

No general conclusions regarding the practical significance of the results should be drawn before more soils and different plants at various growth stages have been examined.

SUMMARY

The principles of radioactive indicators and their adaptation to the study of contact interchange of cations between plant roots and soil colloids are described.

Barley plants containing radioactive potassium retain this isotope against distilled water but release it to salt solutions and clay suspensions. For equal amounts of cations in the nutrient media, the colloids greatly exceed the single-salt solutions in removing radioactive K from plant roots. The outgo of radioactive K from plants increases with concentration of the nutrient media and time of contact.

Experiments with barley plants containing radioactive sodium also show that colloidal clay suspensions are more efficient depleting agents than are salt solutions of corresponding cation concentrations.

These relationships are reversed if direct contact is prevented by placing semipermeable membranes between the roots and the clay particles.

For plants containing radioactive Br anions the clay suspensions remove smaller amounts of the isotope from the roots than do the corresponding salt solutions.

Various experiments are reported which indicate that contact depletion of roots by clay particles is not the result of root injury.

It is shown that the intake of ions by roots is not a uni-directional process; ions of the same species may move into the root and out of the root at the same time.

The results obtained with radioactive elements fully confirm the previously published data obtained with total K analyses of excised barley roots. It is now fairly certain that the theories of chemical soil solution no longer suffice to explain fully the absorption of mineral elements by plants from soils. They must be supplemented by considerations of contact effects.

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THE NATURE OF LATERIZATION AS REVEALED BY CHEMICAL, PHYSICAL, AND MINERALOGICAL STUDIES OF A LATERITIC SOIL PROFILE FROM PUERTO RICO¹

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The exact nature of the laterization process is not definitely known. It is accepted, however, that laterization is a weathering process which takes place in the humid tropics and subtropics and which is characterized by the removal of bases and silica from, and the accumulation of the hydroxides and sesquioxides of aluminum and iron in, the surface horizon (10; 11; 14, p. 366-418; 16; 19; 34, p. 274-337). It has also been pointed out that lateritic soils may be podzolized (34, p. 274-337); that the process of primary laterization may be succeeded by one of resilication (12); that the upward capillary movement of iron in the soil profile (10, 11), and subsoil exposure due to erosion (22, 24), may be factors influencing laterization. That laterization is, perhaps, more strictly a geologic than a pedologic process has likewise been mentioned (15).

Physical and mineralogical studies of lateritic soils have been reported by Bennet and Allison (1, p. 83-84), Fettke and Hubbard (4), Fox (5), Leith and Mead (17, p. 25-44), Mattson and Gustafsson (21), Roberts (26), and Shibuya (32); and chemical studies by various methods have been reported by Harada (8), Hardy (9), and Harrison (12).

Lateritic soils are discussed further by Bonnet (2, 3), Fox (5), Glinka (7), Harrassowitz (10, 11), Imperial Bureau of Soil Science (13), Joffe (14, p. 366-418), Kellogg (15), Marbut (19, 20), Mohr (22), Principi (25), Robinson (27, p. 325-329), Russell (30), and Thorp (34, p. 274-337).

SOIL USED FOR INVESTIGATION

In order to gain further information relative to the laterization process, chemical, physical, and mineralogical studies were made of Catalina clay, the most extensive lateritic soil type of Puerto Rico. This soil, of the mountain and hill lands, which usually occurs where the rainfall is more than 79 inches,

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is derived from andesitic tuff. The depth to rock, ranging from 3 to 40 feet, usually increases with increasing annual rainfall and with the gentleness of the slopes. The surface ranges from rolling to steep, but most of the hills are rounded and are cut by gently sloping ravines. The soil is well drained but is affected by sheet erosion. Like other lateritic soils, Catalina clay exhibits no sharp distinctions between horizons. The surface layer is light red to reddish brown friable clay, the depth of which varies with surface relief from about 4 to 8 inches. The subsurface layer is reddish brown or light red, slightly heavy, friable clay extending to a depth of about 24 inches. Below this is red clay, which continues to great depths. Catalina clay is everywhere acid. It is a poor nitrifying soil, as shown by Bonnet (3) elsewhere. One of the best soils for the growing of coffee, it produces profitable yields of various other crops such as sugar cane, citrus, and pineapple, when properly fertilized.

Six soil samples were taken, May 27, 1937, on Catalina farm, which is at Km. 5.1 of the new Mameyes-Yunque road. The samples were labelled as follows:

- A₁ (0-12 inches)—reddish brown friable clay
- A₂ (12-36 inches)—brownish red friable clay
- B₁ (36-84 inches)—red clay, heavier than A₂ and plastic
- B₂ (84-120 inches)—red clay heavier than B₁
- C₁ (120 inches)—friable rotten parent material
- C₂ (240 inches)—same as C₁

The first two samples were taken with a soil auger in various places of the nearby field; other samples were taken from a fresh cut in the road. The samples were air-dried, sifted through a 20-mesh sieve, and stored in screw-capped jars.

TOTAL SILICA, SESQUIOXIDES, AND BASES IN CATALINA CLAY

Observations were made on the distribution of total silica, sesquioxides, and bases in the profile of Catalina clay. Table 1 contains data for two horizons of the solum and two of the parent material. The results show that the highest contents of total silica and alumina are in the C₁ horizon and the highest content of iron is in the C₂. Results do not point to the leaching of silica from the solum, but they tend to show some accumulation of iron oxide in the A₁ horizon. The parent material is more acid than the solum. The surface soil is well supplied with organic matter.

FREE SILICA AND SESQUIOXIDES IN CATALINA CLAY

As lateritic soils require a more drastic treatment than that of other soils for the removal of free silica and sesquioxides, the following modification, recommended by Truog et al. (35), was used: Five-gram samples, pretreated with 10 per cent hydrogen peroxide to remove organic matter, were given five consecutive treatments with boiling sodium sulfide-oxalic solution for removal of the free iron and aluminum oxides and the free colloidal silica. The extract

was clarified by centrifuging and was saved for determinations of silica, iron, aluminum, and titanium. The residue was extracted further by two consecutive 30-minute treatments with boiling 2 per cent sodium carbonate. The extracts were centrifuged and saved separately for determinations of silica, iron, aluminum, and titanium. The results of these determinations were added to those from previous extracts.

The free iron oxide rises from 13 per cent in the B₂ horizon to 15 per cent in the A₁, and the free alumina rises from 5 to 9 per cent (table 2). This shows a

TABLE 1
Chemical analysis of Catalina clay
Oven-dry basis

HORIZON	DEPTH	pH	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	MnO	TiO ₂	LOSS ON IGNITION	ORGANIC MATTER*
	<i>inches</i>		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A ₁	0-12	5.3	33.70	19.07	31.00	0.18	0.03	0.04	0.33	17.22	6.17
B ₁ †	36-84	5.5	35.40	15.60	30.73	0.51	0.30	0.04	0.86	13.75	0.68
C ₁ †	120+	4.3	38.56	13.86	31.48	0.34	0.67	0.01	0.65	14.22	0.66
C ₂ †	240	4.4	32.70	21.10	26.20	0.10	1.05	0.14	0.19	12.80	0.22

* Determined by Schollenberger's method (31).

† Analyzed by C. J. Rehling, I. C. Gregory, and H. D. Merwin, respectively, soils department, University of Wisconsin.

TABLE 2
Free silica, sesquioxides, and titanite oxide in Catalina clay
Oven-dry basis

HORIZON	DEPTH	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂
	<i>inches</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A ₁	0-12	2.03	15.04	8.87	0.01
A ₂	12-36	3.83	14.94	8.33	0.08
B ₁	36-84	4.05	13.35	6.97	0.04
B ₂	84-120	2.16	13.06	5.21	0.08
C ₁	120+	9.00	11.76	9.20	0.03
C ₂	240	2.85	17.79	4.34	0.10

tendency for the free sesquioxides to accumulate in the upper solum. Results do not point to the leaching of free silica from the solum. The highest contents of free silica and alumina are in the C₁ horizon, and the highest content of iron is in the C₂.

DISTRIBUTION OF THE MECHANICAL SEPARATES IN CATALINA CLAY

Mechanical analyses of lateritic soils are more accurate after the removal of colloidal binding substances which interfere with the dispersion of the fine particles. Organic matter, free iron oxide (hydrated and unhydrated), and

inorganic base-exchange material are involved in this connection. Colloidal silica and free alumina may also be involved. Truog et al. (35) recommend a special type of mechanical procedure after the removal of these binding agents.

The soil fractions were separated by means of a No. 2 International centrifuge, in accordance with the size limits of the Atterberg system: sand (2,000—20 μ), silt (20—2 μ), clay (< 2 μ). The clay was further subdivided at the 0.2 μ size into coarse and fine clay (36).

TABLE 3
Mechanical analysis of Catalina clay
Oven-dry basis

HORIZON	SAND (>20 μ)	SILT (2-20 μ)	COARSE CLAY (0.2-2 μ)	FINE CLAY* (<0.2 μ)	FINE CLAY†	TOTAL CLAY (<2 μ)	ORGANIC MATTER AND MATERIAL LOST IN PROCESS
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A ₁	1.79	3.77	21.42	63.08	37.14	84.50	9.94
A ₂	1.64	2.71	37.12	50.34	23.16	87.46	8.19
B ₁	2.83	8.34	50.68	30.18	5.09	80.86	7.97
B ₂	3.51	12.90	57.12	24.40	3.96	81.52	2.07
C ₁	2.07	18.73	32.58	43.41	13.39	75.99	3.21
C ₂	8.34	13.15	36.91	33.03	7.95	69.94	8.57

* Includes free silica and sesquioxides.

† Does not include free silica and sesquioxides.

TABLE 4
Exchange capacity of the silt and coarse and fine clay fractions of Catalina clay
m.e. per 100 gm. material

HORIZON	SILT	COARSE CLAY	FINE CLAY	SOIL
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
A ₁	4.4	6.9	9.9	8.4
A ₂	6.0	7.1	5.5	8.1
B ₁	6.3	8.7	6.2	8.6
B ₂	9.3	11.2	2.3	6.3
C ₁	8.9	9.8	7.9	9.9
C ₂	9.4	11.8	10.2	6.6

Table 3 shows the distribution of the mechanical separates in the various horizons of Catalina clay. The clay content of the soil profile is very high, varying between 70 per cent in the C₂ horizon and 87 per cent in the A₂. The silt fraction decreases going upward from the C₁ to the A horizon. Fine clay decreases markedly and coarse clay increases markedly going upward from the C to the B horizon; above that, the coarse clay decreases and the fine clay increases regularly from the B to the A horizon.

EXCHANGEABLE BASES AND AVAILABLE NUTRIENTS IN CATALINA CLAY

The extent to which the weathering process has affected the exchangeable bases in the Catalina clay profile is shown in tables 4 and 5.

The exchange capacity of the soil profile is rather low, varying between approximately 6 m.e. in the B₂ horizon and 10 m.e. in the C₁. The exchange capacity of the silt and coarse clay fractions increases, and that of the fine clay decreases with solum depth (table 4).

Bases, especially lime, are distributed more or less uniformly in the first three horizons; about three-fourths of the exchange material is saturated equally with calcium and hydrogen. The exchangeable hydrogen is higher in the C₁ horizon than in the C₂ (table 5). There is a sharp pH change between the andesitic tuff and the soil parent material; the pH of the former is 8.2 and that of the latter is 4.4.

TABLE 5

Exchangeable bases and hydrogen, total exchange capacity, and pH of Catalina clay
m.e. per 100 gm. dry soil

HORIZON	DEPTH	K	Ca	Mg	H	TOTAL EXCHANGE CAPACITY	pH
	<i>inches</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	
A ₁	0-12	0.19	3.40	1.52	3.29	8.40	5.3
A ₂ *	12-36	0.13	3.33	1.01	3.63	8.10	6.4
B ₁ *	36-84	0.09	2.80	1.72	3.99	8.60	5.5
B ₂	84-120	4.4
C ₁ *	120+	0.19	0.64	1.22	7.85	9.90	4.2
C ₂ *	240	0.07	0.75	0.91	4.87	6.60	4.4
D	Andesitic tuff	8.2

* Analyzed by D. M. Batson, C. J. Rehling, I. C. Gregory, and H. D. Merwin, respectively, soils department, University of Wisconsin.

SPECIFIC GRAVITY SEPARATION OF THE MINERALS IN CATALINA CLAY

The minerals of the silt and coarse clay fractions were separated into specific gravity groups as recommended by Pearson and Truog (23). Mixtures of symmetrical tetrabromoethane (sp. gr. 2.98) and nitrobenzene (sp. gr. 1.20) were used for the separation of minerals.

The specific gravity separations were made in accordance with the following scheme:

SPECIFIC GRAVITY GROUP	MINERAL GROUPS
> 2.98	Iron minerals, muscovite, biotite, zircon, rutile
2.70-2.98	Talc, plagioclase
2.50-2.70	Quartz, plagioclase and potash, feldspars, chlorite
< 2.50	Clay minerals

The results, in table 6, show that the bulk of the silt fraction is comprised of minerals the specific gravities of which are less than 2.7. The heavier

minerals are evenly distributed between the specific gravity groups 2.70–2.98 and >2.98. In the A₁, A₂, and B₁ horizons the lighter minerals are evenly distributed between the specific gravity groups 2.5–2.7 and <2.5. In the B₂ and C₂ horizons, however, the largest percentage of the minerals is in the specific gravity group 2.5–2.7; and in the C₁ horizon, in the specific gravity group <2.5.

IDENTIFICATION OF THE MINERALS IN CATALINA CLAY

The minerals were identified qualitatively by petrographic methods. Observations made on a thin section of the consolidated parent rock of Catalina clay revealed the following minerals: abundant augite and serpentine, appreciable quantities of calcite and chlorite, and little andesine and glass. Observations were also made of the sand and specific gravity groups of the silt and coarse clay from the various horizons in the Catalina clay profile, according to the following scheme:

TABLE 6
Specific gravity separates of the silt (2–20 μ) fraction of Catalina clay

HORIZON	SP. GR. >2.98	SP. GR. 2.70–2.98	SP. GR. 2.50–2.70	SP. GR. <2.50	LOST IN MAKING SEPARATIONS
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A ₁	3.5	4.3	42.8	39.2	10.2
A ₂	5.8	2.8	45.4	42.0	4.0
B ₁	5.2	2.4	42.0	42.4	8.0
B ₂	3.2	2.2	60.8	24.4	9.4
C ₁	2.8	2.4	28.4	49.6	16.8
C ₂	4.4	3.2	56.8	30.4	5.2

Temporary mounts were made in an oil having the index of quartz, 1.544. In studying the minerals by means of the petrographic microscope, the following observations were made, where possible, to differentiate the various mineral species: color, refringence, birefringence, pleochroism, cleavage, form, twinning, extinction angles, interference figures, and signs. The approximate refractive indexes of the minerals were found by making temporary mounts in oils of different indexes. The color of opaque minerals was observed by means of reflected light. For details of the technic, description, and optical properties of minerals, the reader is referred to Fry (6), McIlvaine-Luquer (18), Rogers and Kerr (28), and Winchell (37).

Table 7 contains data of the minerals identified in the silt fractions from the various horizons in the Catalina clay profile. A kaolinlike mineral was identified on the basis of the suggestion of Ross and Kerr (29) that it, unlike the other stained minerals, is pleochroic when stained with dyes. A malachite green solution, used as a dye, was prepared by diluting one drop of a 5 per cent solution with 20 cc. of distilled water. The colors of the stained kaolinlike mineral turned from green to plum with rotations of the microscope stage.

Muscovite, quartz, and serpentine, the most abundant minerals, are largely in the specific gravity group 2.5–2.7 but are also present in the other groups. The C₂ horizon, however, contains less muscovite and quartz than the other horizons. The accessory minerals consist largely of the heavy minerals: rutile, augite, leucoxene, zircon, magnetite, sericite, and calcite; and of the lighter minerals: andesine, glass, gibbsite, and a kaolinlike mineral. The

TABLE 7

Minerals identified in the specific gravity groups of the silt fraction of Catalina clay*

HORIZON	SPECIFIC GRAVITY GROUP	RTILE	AUGITE	LEUCOXENE	ZIRCON	MAGNETITE	CHLORITE	MUSCOVITE	QUARTZ	EPIDOTE	SERPENTINE	SERICITE	CALCITE	TALC	GLASS	ANDESINE	GIBBSITE	KAOLINLIKE MINERAL
A ₁	>2.98	xx	x	x	x	x
A ₂	xx	x	x	x	x	x	x	Tr.	Tr.
B ₁	xx	x	x	x	x	x	x	Tr.	Tr.
B ₂	xx	...	x	x	x	x
C ₁	x	x	x	x	x
C ₂	x	x	x
A ₁	2.70–2.98	x	x	x	...	x	x	x
A ₂	x	x	x	...	x	x	x
B ₁	x	x	x	...	x	x	x
B ₂	x	x	x	...	x	x	x
C ₁	x	x	x	...	x	x	x
C ₂	xx	xx	x	...	xx	...	x
A ₁	2.50–2.70	xxx	xxx	...	xxx	x
A ₂	xxx	xxx	...	xxx	x
B ₁	xxx	xxx	...	xxx	x
B ₂	xxx	xxx	...	xxx	x
C ₁	xxx	xxx	...	xxx	x
C ₂	x	...	xxx	x
A ₁	<2.50	x	x	x	...	x	x
A ₂	x	x	x	...	x	x
B ₁	x	Tr.	...	x	Tr.	x	...	Tr.	x
B ₂	x	Tr.	...	x	Tr.	x	...	Tr.	x
C ₁	x	Tr.	...	x	Tr.	x	...	Tr.	x
C ₂	x	Tr.	...	x	Tr.	x	...	Tr.	x

* x = little; xx = appreciable; xxx = abundant; Tr. = trace.

heavier minerals and gibbsite are more abundant in the solum than in the parent material.

DISCUSSION OF RESULTS WITH CATALINA CLAY

The consolidated parent rock of Catalina clay, according to its mineralogical composition, is an andesitic tuff. It contains abundant augite, which is essen-

tially a metasilicate of lime, magnesia, and ferrous iron, plus silicates of ferric iron and alumina. Augite is a ferromagnesian mineral and an important member of the pyroxene group. The presence of the secondary minerals serpentine, calcite, and chlorite indicates that this rock is a product of metamorphism. The plagioclase feldspar which occurs in this rock is andesine, which has been considerably altered through weathering processes. A characteristic of this rock is the absence of quartz.

This andesitic tuff is basic in reaction, pH 8.2 (table 5). It has given rise to an acid parent material (pH 4.4), that is, the C₂ horizon, rich in clay, total magnesia, and free iron oxide and alumina, but poor in free silica (tables 1 and 2). In passing from solid rock to parent material of Catalina clay, laterization is already pronounced and may thus be considered to be very largely a geologic process rather than a soil-building process. The weathering of the andesitic tuff released a large amount of magnesium, calcium, and sodium. The alkaline reaction of the medium in the early stages favored the precipitation of the soluble sesquioxides and the solution of silica. The presence of considerable easily soluble sodium in the early stages of weathering was probably a factor in increasing the solubility of silica. The humid climate provided sufficient precipitation to wash away from the soil parent material a large amount of bases and soluble silica.

The C₂ horizon has the highest contents of total and free iron oxide. The C₁ horizon has the highest contents of free silica, free alumina, and exchangeable hydrogen. The B₂ horizon has the highest content of coarse clay. These high contents are the result of the hydrolysis of augite in the B₂ and C₁ horizons. This is indicated by the absence of augite in these two horizons. The presence of this mineral in the A₁, A₂, and B₁ horizons, on the other hand, may be due to the formation of secondary augite in those horizons or to less favorable conditions for the hydrolysis of augite. Ferrous iron is probably set free in the B₂ and C₁ horizons, and, because of poorer conditions of oxidation at that depth, it moves down to the lower portion of the C₂ horizon where, because of less acid conditions, it is precipitated and oxidized as hydrated ferric oxide.

The percentages of free and total iron oxide and alumina rise regularly from the B₂ to the A₁ horizons. The percentages of free and total iron oxide rise also from the C₁ to the B₂ horizons. There is little evidence of the leaching of silica from the solum (tables 1 and 2). Sesquioxides have accumulated in the upper horizon, not solely because silica has been leached in the earlier stages of rock weathering, but because of further dehydration of hydrated sesquioxides in the upper solum where dryness is more effective because of higher temperatures. This is corroborated by the presence of magnetite in the upper three horizons and by its absence in the lower horizons. Catalina clay is a permeable soil because the large amount of hydrated and nonhydrated sesquioxides in the clay complex tend to keep it flocculated.

The rapid mineralization of organic matter is not a factor in laterization. The bulk of the soluble silica was leached, not because of the alkaline hydrolysis

resulting from the complete decomposition of organic matter, but because it was removed during the laterization of the andesitic tuff. The rapid mineralization of organic matter is, however, a factor in supplying bases for the solum.

The silt and coarse clay increase, and the fine clay decreases, both in quantity and exchange capacity, with solum depth. This is to be expected because of the more active disintegration of coarser particles in the A horizon. The active bases in the upper solum tend to flocculate the exchange material of the fine clay. As a result of this, much of the exchange material of the fine clay probably precipitates in the upper solum. The exchange capacity of the soil as a whole (table 4) appears to be unaffected by this process.

The exchange capacity of this soil is very low, only 6-10 m.e. A kaolinlike mineral identified in the quartz fraction of coarse and fine clay portions may be the seat of this exchange capacity. This kaolinlike mineral, however, was not found to be so abundant as muscovite, which is known to have slight but appreciable exchange capacity. There is a difference of 3 m.e. in the exchange capacity of horizons C₁ and C₂, in favor of the former (table 4), and muscovite was found to be more abundant in the former (sp. gr. 2.5-2.7, table 7). The material which gives rise to the exchange capacity of this soil thus appears to be a kaolinlike mineral and muscovite.

It is rather significant that muscovite is largely in the specific gravity group 2.5 to 2.7. It is also present in the specific gravity group of less than 2.5. According to Winchell (37) the specific gravity of muscovite ranges between 2.76 and 3.00. It seems, therefore, that hydration has affected this residual mineral. Muscovite has also been partly altered to sericite, a secondary muscovite, in all the soil horizons except the C₂. Traces of talc with a specific gravity of less than 2.5 were found in the B and C horizons. Talc was also found in the C₂ horizon as a heavy mineral having a specific gravity greater than 2.98. The specific gravity of talc, according to Winchell (37), ranges between 2.7 and 2.8. It seems, therefore, that the talc identified here as such has been considerably affected by weathering.

The bulk of the silt fraction is made up of the lighter minerals (table 6), largely muscovite, quartz, and serpentine (table 7). It must be pointed out, however, that the light mineral gibbsite and the heavy iron minerals were less abundant in the material examined, because most of the hydrated alumina minerals and all of the hydrated iron oxide minerals were destroyed, previously, by the drastic sodium sulfide-oxalic acid and sodium carbonate treatments. Magnetite and rutile were found to be present because they are resistant to the chemical treatment. Diaspore, Al₂O₃, was found to be absent in the soil profile. Chlorite and calcite are distributed throughout the profile. Quartz is very abundant throughout the soil profile except in the C₂ horizon. It is present as secondary quartz, since the original andesitic tuff had no quartz. A little andesine is present in all of the horizons except the C₂.

Catalina clay is a lateritic soil having as constituent minerals hydrated iron



oxides, gibbsite, muscovite, secondary quartz, serpentine, and, as accessory minerals, rutile, augite, leucosene, zircon, magnetite, chlorite, sericite, calcite, glass, andesine, a kaolinlike mineral, and traces of talc and epidote. The hydrated iron oxides and gibbsite constitute from 18 to 24 per cent of the soil body. The accumulation of these resistant or inert minerals points to a severe weathering process.

To gain further information relative to the contention that laterization is largely a geologic process rather than a soil-building process, certain additional tests were made of soil profile samples of other lateritic soils from Puerto Rico, and of the parent material of the Catalina clay as well as that of two other lateritic soils and also of a nonlateritic soil.

REACTION OF VARIOUS HORIZONS OF OTHER LATERITIC SOILS

It was considered of importance to determine the effect of weathering in the profile of other lateritic soils. Determinations of pH, for the various soil horizons, were made colorimetrically with Truog's soil reaction tester. Table 8 contains pH data for the profile of seven lateritic soils from Puerto Rico located in the humid northern section of the Island. The data indicate that the rocks are neutral or alkaline, whereas the parent soil materials (horizon C₁) have, in most cases, already become strongly acid.

SOLUBILITY OF SILICA IN PARENT ROCKS OF LATERITIC AND NONLATERITIC SOILS

The following tests were made to find out whether soluble silica is released more rapidly from rocks which give rise to lateritic soils than from rocks which do not give rise to these soils.

Three consolidated parent materials of upland lateritic soils and one of a nonlateritic soil, in Puerto Rico, were chosen for this work. The lateritic soils are represented by an andesitic tuff, a serpentine rock, and a granitoid or granitlike rock; and the nonlateritic soil is represented by a quartz diorite. The rocks were ground in a steel mortar and sifted through a 160-mesh sieve. The parent material (horizon C₂) of Catalina clay was also included in the tests. In each case, a 0.1-gm. portion of the material was transferred to a liter Florence flask, and then a liter of distilled water was added. To a second similar set, carbonated water was added in place of distilled water. The flasks were stoppered and shaken for 1 day in an end-over-end shaker, after which portions of the supernatant liquid in each instance were clarified by centrifuging with an angle head for 10 minutes at 3600 r. p. m.

Soluble silica was then determined colorimetrically by means of the yellow color which developed on the addition of molybdate ions in a slightly acid solution as described by Snell (33, p. 517-525). It was found that the effect due to phosphorus is kept under control when the solution is brought to pH 1.5. The procedure used was as follows: A volume of 100 cc. of extract was evaporated to about 10 cc.; the pH was brought to 1.5 by adding 0.05 *N* HNO₃;

the color was then developed by adding 2 cc. of a 10 per cent solution of ammonium molybdate; and dilution was brought to 50 cc. for final comparison of color with that of a standard silica solution, in Nessler tubes. This method was checked gravimetrically, 500 cc. of the extract, which served also for the determination of soluble salts, being used. Phosphorus was also determined colorimetrically by the molybdate-blue method as a further check on its possible interference. The pH of the extracts was determined colorimetrically. The presence of iron was tested by evaporating a 50-cc. aliquot of the extract to about 5 cc., acidifying with two drops of HCl (1-1), and then adding two drops of a 2 per cent solution of potassium thiocyanate. Results, reported

TABLE 8
Reaction of different horizons of a number of lateritic soils from Puerto Rico

COTO CLAY			MATANZAS CLAY			ESPINOSA SANDY CLAY			BAYAMON CLAY		
Depth	Horizon	pH	Depth	Horizon	pH	Depth	Horizon	pH	Depth	Horizon	pH
<i>inches</i>			<i>inches</i>			<i>inches</i>			<i>inches</i>		
0-7	A	5.5	0-12	A	7.3	0-8	A	5.5	0-10	A	5.2
7-17	B	6.0	12-21	B ₁	6.7	8-15	B	4.3	10-28	B	6.0
.....	21-34	B ₂	6.5
17-40	C ₁	8.0	34-48	C ₁	6.3	15-36	C ₁	4.3	28+	C ₁	4.5
Limestone	D		Limestone	D		Limestone	D		Limestone	D	

NIPE CLAY			ALONSO CLAY			ALONSO CLAY, SMOOTH PHASE		
Depth	Horizon	pH	Depth	Horizon	pH	Depth	Horizon	pH
<i>inches</i>			<i>inches</i>			<i>inches</i>		
Iron nodules at surface	..	5.7
0-36	A	5.3	0-18	A	4.8	0-10	A	6.2
36-56	B ₁	5.5	18-24	B	4.8	10-24	B	6.0
56-68	B ₂	6.0
68+	C ₁	6.2	24	C ₁	4.8	24-36	C ₁	4.4
Serpentine rock	D	7.8	Purple igneous rock	D	7.0	Purple igneous rock	D	7.0

in table 9, indicate that the silica of the parent rocks of the lateritic soils investigated was more subject to solution and leaching in water than was the silica of a parent rock (quartz diorite) of a nonlateritic soil. In carbonated water, however, the silica of the latter rock was as soluble as that of the former rocks. But carbonated water was more effective in extracting iron from parent rocks of lateritic soils bearing ferromagnesian minerals than from a parent rock (quartz diorite) of a nonlateritic soil.

GENERAL DISCUSSION

The pH data reported in table 8 indicate that the parent rocks of lateritic soils, in general, are basic in reaction but that some may have a neutral reac-

tion. The disintegrated parent materials (horizon C₁) are generally acid in reaction, except for Coto clay which is alkaline because of the presence of limestone particles. The disintegrated parent materials of these soils appear to be high in sesquioxides, as is that of Catalina clay.

Results given in table 9 indicate that the silica of the parent rocks of the lateritic soils investigated is more subject to solution and leaching in water than is the silica of a parent rock (quartz diorite) of a nonlateritic soil. In carbonated water there was not much difference in solubility of silica between the two parent-rock types, but it must be remembered that the percolating waters of these soils are probably, for the most part, low in their content of carbonic acid. The solvent action of the carbonated water was greater than that of the water alone in all cases, with the exception of serpentine. The water extracts had a pH around 5.2, whereas the carbonated extracts had a

TABLE 9

Solubility in water and in carbonated water of silica, phosphorus, iron, and total constituents of parent rock materials of lateritic and nonlateritic soils and pH of extracts

PARENT MATERIAL	WATER EXTRACT						CARBONATED WATER EXTRACT							
	pH	Dissolved					pH		Dissolved					
		Total constit- uents	SiO ₂		P	Fe	Before boiling	After boiling	Total constit- uents	SiO ₂		P	Fe	
			Colori- metrically	Gravi- metrically						Colori- metrically	Gravi- metrically			
per cent	per cent	per cent	per cent	per cent										
Andesitic tuff.	5.2	6.8	1.2	1.6	0	0	4.6	6.6	19.2	3.2	4.8	0.016	little	
Serpentine rock.	5.4	10.0	4.8	4.4	0	0	4.2	6.8	6.8	3.8	1.4	0.0	0	
Granitoid.	5.0	4.6	1.0	1.0	0	0	4.2	6.2	8.0	0.4	2.0	0.034	little	
Quartz diorite.	5.2	3.6	0.0	0.0	0	0	4.2	5.6	14.2	3.5	4.2	0.024	trace	
Catalina C ₂	5.2	2.8	2.2	2.0	0	0	4.2	6.0	5.0	2.4	2.6	0	0	

pH around 4.2. Boiling the latter increased the pH somewhat. Carbonated water extracted also more iron from two parent rocks (andesitic tuff and granitoid) of lateritic soils than from the parent rock (quartz diorite) of a nonlateritic soil. Carbonated water was found to be ineffective in extracting iron and phosphorus from the serpentine rock.

A better picture of the rocks is obtained by studying their mineralogical composition. The andesitic tuff has already been discussed. The serpentine rock contains mainly serpentine, bastite, minute grains of magnetite and chromite, and secondary iron oxides, principally limonite. The granitoid contains quartz, feldspar, biotite, and muscovite. The quartz diorite contains abundant quartz and also plagioclase feldspar and hornblende. The quartz diorite rock is basic in reaction, pH 8.0, and gives rise to traces of iron in the carbonated water extract. It does not weather into a lateritic soil, however,

because the bulk of its silica is not readily soluble. The granitoid rock is neutral in reaction, pH 7.0, and gives a test for iron in the carbonated water extract. It weathers, under humid tropical conditions, into a lateritic soil because it contains abundant bases and considerable easily soluble silica. The serpentine rock is basic in reaction, pH 7.8, but does not give a test for iron in the carbonated water extract. This rock is derived from a peridotite containing augite and olivine, ferromagnesian minerals that weathered into serpentine, magnetite, chromite, and secondary iron oxides, principally limonite. Laterization of serpentine releases a large amount of bases and soluble silica, which are washed away by the tropical rains. The hydrated and non-hydrated iron oxides remain in place to form a part of the parent material of the Nipe laterite.

Under humid tropical conditions, limestone weathers into lateritic soils when it contains considerable hydrated or nonhydrated oxides of iron and is low in silica. Laterization of limestone releases soluble calcium bicarbonate and leaves in place the oxides of iron. As the silica content increases, laterization is retarded because part of the lime may remain in place as insoluble calcium silicate.

The additional tests made on the reaction of various horizons of seven lateritic soils and on the water solubility of silica in parent materials of three lateritic soils and of a nonlateritic soil confirm the contention that laterization is largely a geologic process rather than a pedologic process.

Since laterization thus appears to be largely a process of mere physical and intense chemical weathering rather than a soil building or so-called pedologic process, and since there are no true horizons of eluviation and illuviation, these lateritic soils might better be looked upon as having only an A horizon consisting of the A₁ which contains some organic material and which grades into the A₂ horizon, extending virtually to the solid rock. The podzolization process is so limited under intense laterization that typical soil profiles are not usually developed.

SUMMARY

The nature of laterization has been investigated as revealed by chemical, physical, and mineralogical studies in the various horizons of a 20-foot profile of Catalina clay, an upland residual lateritic soil from Puerto Rico. The free silica and sesquioxides were extracted by special methods prior to the mechanical separations into sand, silt, and coarse and fine clay fractions. The silt and coarse clay were further separated into convenient specific gravity groups to facilitate the identification of the minerals by petrographic methods. Additional tests were made on the reaction of various horizons of seven lateritic soils and on the solubility of silica in parent rocks of three lateritic soils and of a nonlateritic soil. The results obtained may be summarized as follows:

In the formation of Catalina clay, an andesitic tuff, which is a basic rock rich in ferromagnesian minerals and containing some plagioclase feldspar, has been laterized into an acid

parent material rich in clay, total magnesia, and free iron oxide and alumina, but poor in free silica and bases. The weathering of the rock released a large amount of magnesium, calcium, and sodium. The alkaline reaction of the rock and of freshly weathered material has favored the precipitation of the sesquioxides and the solution of silica. The presence of considerable easily soluble sodium in the early stages of weathering was probably a factor in increasing the solubility of silica. The humid climate provided sufficient precipitation to wash away from the parent soil material the bulk of bases and soluble silica resulting from the laterization process.

It was found by chemical means that free iron oxide and free alumina constitute 18 to 24 per cent of the soil body of Catalina clay.

Sesquioxides have accumulated in the upper horizon of Catalina clay, not solely because silica has been leached in the earlier stages of rock weathering, but because of further dehydration of hydrated sesquioxides in the upper solum where oxidation conditions are better. Catalina clay is a permeable soil because the large amount of hydrated and nonhydrated sesquioxides in the clay complex tends to keep it flocculated.

The clay content of Catalina clay is very high, varying between 70 per cent in the C₂ and 87 per cent in the A₂ horizon. The silt and coarse clay increase somewhat, and the fine clay decreases, with solum depth. This is to be expected in view of the more active disintegration of silt and coarse clay particles in the upper solum.

Rapid mineralization of organic matter is not an important factor in laterization but is a factor in supplying bases for the solum.

The pH of Catalina clay rises from 4.4 in the parent soil material to 6.4 in the A₂ and 5.3 in the A₁ horizon. About three-fourths of the exchange capacity of the solum is saturated equally with calcium and hydrogen.

The exchange capacity of Catalina clay is rather low, only 6 to 10 m.e. The exchange capacity of the silt fraction increases from 4 to 9 m.e. and that of the coarse clay from 7 to 11 m.e., with solum depth, whereas that of the fine clay decreases from 10 to 2 m.e. It appears, therefore, that the active disintegration of the silt and coarse clay particles in the upper solum lowers also their exchange capacities. The active bases in the upper solum tend to flocculate the exchange material of the fine clay. As a result, much of the exchange material of the fine clay is probably deposited in the upper solum. The low exchange capacity of the soil as a whole is due either to a small amount of true base exchange material or else to material like muscovite, and the kaolinlike minerals, which have appreciable but low exchange capacity.

Specific gravity separations of the silt fraction of Catalina clay revealed that the bulk of the soil minerals have specific gravities ranging from 2.5 to 2.7.

The constituent minerals of the solum of Catalina clay are hydrated iron oxides, gibbsite, muscovite, secondary quartz, and serpentine. The accessory minerals are rutile, augite, leucoxene, zircon, magnetite, chlorite, sericite, calcite, glass, andesine, a kaolinlike mineral, and traces of talc and epidote. The accumulation of these resistant or inert minerals points to a severe weathering process.

In the eight lateritic soil profiles investigated, it was found that the parent rocks were neutral or alkaline, whereas the parent soil material (horizon C) had, in most cases, already become strongly acid and highly laterized, indicating that the laterization process is largely geologic rather than pedologic.

The silica of the parent rocks of the lateritic soils investigated was more subject to solution and leaching in water than was the silica of a parent rock (quartz diorite) of a nonlateritic soil. In carbonated water there was not much difference, but it must be remembered that the percolating waters of these soils are probably, for the most part, low in their content of carbonic acid.

Laterites are products of humid tropical weathering of rocks which are usually basic in reaction, resulting in acidic material high in free sesquioxides, low in free silica and exchange capacity, very permeable to water and air, and, in many instances, of great depth, but exhibiting little or no differentiation into soil horizons.

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EXPERIMENTS WITH BORON ON SOME NEW JERSEY SOILS¹

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The numerous reports concerning the physiological importance of boron and its use in preventing certain diseases of plants, the recent widespread interest in its use in connection with fertilizers, and the need for definite information in regard to how crops respond to boron treatments on different types of soil, prompted this investigation. The object was to determine whether or not any soil and crop conditions in New Jersey require the use of boron, and, if the work showed increased yields from the use of boron, to make a careful study of the rate at which it should be used.

HISTORICAL

Since 1910 when Agulhon (1) demonstrated that wheat, oats, and radish require some boron for their normal development, numerous workers have shown the importance of this element in plant production. Maze (32), Warrington (47), Brencley (6), Somner and Lipman (44), Somner and Sorokin (45), Johnston and his associates (22, 23, 24, 25), McHargue and Calfee (26), and McMurtrey (30) were among the later workers who were able to demonstrate that a wide variety of green plants are unable to complete their life cycle without at least a trace of boron.

Agulhon (1) and later Brencley and Warrington (8) tried to explain the function of boron in the plant by noting the amounts of boron used, whereas others such as Haas and Klotz (16), Somner and Sorokin (45), Warrington (47), Johnston (22), Brencley and Thornton (7), and Johnston and Dore (24) studied the cytological changes brought about by boron deficiencies in an effort to explain the role of boron. Warrington (47) and McHargue and Calfee (26) have attempted, without success, to substitute other elements for boron. More recently Schmucker (39) tried to explain the function of boron from experiments performed with pollen grains. Although these investigators have amassed many useful data, a completely satisfactory answer as to exactly why plants need boron is still lacking.

It was Brandenburg (5) who first demonstrated that a crop under field conditions could be suffering from a lack of boron. His work proved that dry or crown rot of sugar beets could be prevented by a sufficient supply of boron. This work has been substantiated by Rowe (37), Hanley and Mann (17), and Raleigh and Raymond (36). Hill and Grant (20) and Obrien and Dennis (34), working with sand and solution cultures, and later Macleod

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and Howatt (29) and Snyder and Donaldson (42), working with soil, have shown that boron is necessary to prevent black heart of turnips. The physiological disorders, drought spot and corky core, of apples have been treated successfully by McLarty (27), Hill and Davis (19), Degman and his associates (12), and Burrell (9), by applying a compound of boron to tree or soil. By addition of boric acid to the soil, McMurtrey (31) has succeeded in curing a disease of tobacco similar in appearance to the disease known as "topziekte." Purvis and Ruprecht (35) have found that borax will prevent the appearance of a physiological disease of celery known as cracked stems. Dearborn and his co-workers (10, 11) and Hartman (18) point to the fact that boron is essential in preventing browning of cauliflower. Besides the aforementioned diseases, a disease of spinach (18) and the yellows of alfalfa (28) may be due to an insufficient supply of boron.

It has been pointed out by various workers that certain conditions in the soil help to bring about boron deficiencies. Hill and Davis (19) found that corky core and drought spot of apples were prevalent on high carbonate lime soils. Obrien and Dennis (34) came to the same conclusion about black heart of turnips. Bobko and his co-workers (4) have shown that the ill effects of overliming can be corrected by additions of boron to the soil. Naftel (33) found that whenever he completely saturated the soil with calcium he obtained boron deficiencies. Hartman (18) strikes a discordant note by claiming that browning of cauliflower occurs more often in soils which are distinctly acid. Other factors which have been suggested as influencing boron availability are moisture and nitrogen level.

Several reasons have been advanced to explain why soils under field conditions show boron deficiency. Dennis and Obrien (14) think that soils originally low in boron or soils which have been cropped and leached continuously without replacement of boron may become boron deficient. Solunskaya (43) claims that the extensive development of leaves of plants grown on soils of high pH require a large amount of boron, and that soils having a high pH are most likely, therefore, to show boron deficiencies. Bobko and his co-workers (4) claim that boron deficiency is not due to chemical precipitation of boron but that boron is fixed by organisms taking part in the denitrification process which is hastened at the higher pH. Naftel (33), without presenting any specific data on this point, also discounts chemical precipitation and is inclined to agree with Bobko. Hartman (18) fails to suggest any reason why he found a greater number of boron-deficient plants on soils of low pH than on soils of high pH.

The effect of boron upon plants has been studied from another viewpoint, that of excesses or toxicity. Blair (2) and Blair and Brown (3) have shown the injurious results caused by excess borax, and Schreiner and his co-workers (38) have shown the ill effects of excess borax carried by certain potash salts. Eaton (15) and Scofield and Wilcox (40) have studied the effects of excess boron in irrigation waters. Eaton (15), Schreiner and his co-workers (38), and Weber (48) have described the boron toxicity symptoms of various plants, and Weber has made a detailed study of the internal anatomical changes produced by a toxic concentration of boron.

MATERIALS AND METHODS

Soils

Types and location. For pot experiments, soils were collected as follows: Sassafras loam from two different locations on the College Farm, Sassafras sandy loam from the vicinity of Bridgeton, Sassafras sand from the vicinity of Old Bridge, Collington sandy loam from the vicinity of Matawan, Colts Neck loam from the vicinity of Colts Neck, Dunellen sandy loam from Dunellen, and Hagerstown silt loam from the vicinity of High Bridge.

Methods of handling. The experiments with the different soils were performed in the greenhouse because of the ease in controlling conditions and in handling several soil types. In each case the soil was screened through a sieve of $\frac{1}{4}$ -inch mesh and then thoroughly mixed before being placed in glazed pots. These pots, some of which were of 2-gallon capacity and others of 1-gallon capacity, had no drains.

Soil treatment

Lime, fertilizer, and borax applications to these soils were calculated on the weight basis, assuming 2,000,000 pounds of soil to the plowed acre.

Fertilizers. The fertilizers applied consisted of a solution of $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 . Chemically pure salts were used to exclude the possibility of introducing boron with the fertilizers. An application equivalent to 1000 pounds of a 5-5-7 per acre for lettuce, beans, and radishes, and equivalent to 500 pounds for oats, was made before planting.

Lime. Because of reports of some response to boron applications on limed soils, the original plan was to adjust each type of soil to two different pH levels: the soil of section A to be at the field pH or adjusted to a relatively low pH, corresponding to that of soils in the state receiving no lime or very small applications; and the soil of section B to be limed to a pH of 6.0-6.6, corresponding to that of soils limed in accordance with good practice.

This plan was followed in the study of Collington sandy loam, Colts Neck loam, and Hagerstown silt loam (experiment 1). As the original pH of both samples of Sassafras loam was above 6.0, no attempt was made to study this soil at two pH levels. A further deviation from the plan followed in the raising of the pH of both sections of Sassafras sand above 7.0. A favorable response to borax in both sections of this soil suggested the possibility of obtaining beneficial results at high pH levels. The original plan was therefore modified to provide for the liming of section B to a pH above 7.0. This modified plan was followed in a second experiment with Hagerstown silt loam and in the study of Sassafras and Dunellen sandy loams.

The lime applied was a high calcium hydrated lime. In all cases it was mixed thoroughly with all the soil several days before planting of the crop.

Borax. Boron was supplied in the form of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$). This was dissolved in distilled water, and after it was applied the soil was flooded with distilled water to give an even distribution. The borax treatments were applied after the planting of each crop.

Other trace elements. No effort was made to supply any of the other trace elements, since it was assumed that the soil could supply these.

Growing of crops

In each section of the various soils, crops were grown with and without borax in triplicate pots. Crops were grown as season and conditions permitted.

On some soils several crops were grown. In watering plants only distilled water was used, each pot receiving the same amount. All crops were grown until they reached market size.

Statistical treatment

All yield values were treated statistically to enable the evaluating of response to treatment. In all treatments the following values were obtained: the mean (M_n) and its probable error (P.E.) and the standard deviation (σ) and its probable error (P.E.).

Whenever the significance of differences between means was in question, the existence of significance was determined by the Holinger (21) test using the formula $P.E. (M_{n_1} - M_{n_2}) = \sqrt{(P.E. M_{n_1})^2 + (P.E. M_{n_2})^2}$. The yields were classified as significant when the difference between the means of yields of the two treatments was at least four times the P.E. ($M_{n_1} - M_{n_2}$).

Analysis of plant material

The boron content of a number of plants was determined, to answer some of the questions raised. All plant samples were dried in the oven at about 70°C. and then were ground in a Wiley mill until the material would pass through a 1-mm. sieve. Composite samples of plants grown in the three pots of soil receiving the same treatment were prepared by the method of Delong (13) and were analyzed by the method of Smith (46), with the following exceptions: In most cases only 5-gm. samples, and in no case more than 10 gm., of oven-dried material were used. The HCl washings of the ignited material were not made up to 50 cc., but the boron content was determined by using an aliquot of 1 cc. from the combined filtrates. If the boron content was found too high for reading, the combined filtrates were diluted until 1 cc. of solution gave a boric acid concentration which could be determined by comparison with the set of standards (0.005 mgm.-0.04 mgm. of boric acid). In samples of plant material grown on soil not treated with borax no further dilution of the filtrates was necessary. In plants grown on soils treated with borax, however, it was found necessary to dilute the combined filtrates. Although Smith (46) claims that the reaction necessary to determine the boric acid takes place in 5 minutes, it was found necessary to allow all samples, after sulfuric acid and quinalizarin were added, to come to room temperature before reading. All readings were taken, therefore, after the samples had been standing for 30 minutes.

TECHNIC AND RESULTS OF INDIVIDUAL EXPERIMENTS

Sassafras loam

In one group of pots containing Sassafras loam, a crop of Scarlet Globe radish was grown on soil with 0, 10, and 20 pounds of borax per acre. This crop was followed by Big Boston lettuce, the borax treatments being repeated. In another group of pots, receiving similar borax treatments, a crop of Keystone

oats was followed by a crop of Bloomsdale Long Standing spinach. Results are reported in table 1.

The results definitely show that radish, lettuce, oats, and spinach grown on this soil do not respond favorably to boron treatment. Applications of borax gave no increase in yield, and characteristic toxicity symptoms appeared on all crops grown with the 20-pound borax treatment. Despite these visual symptoms, lettuce was the only crop which gave a significant decrease in yield.

Sassafras loam from plot 7B

To study the response to borax by crops grown on a soil which had not been fertilized for many years, soil was obtained from plot 7B of the nitrogen availability series of field plots at the New Jersey Agricultural Experiment Station. This plot had received no fertilizer for 30 years but had received an application of 4000 pounds of limestone per acre every 5 years, except 1933 when the application of limestone was omitted. With the exception of slight modifications,

TABLE 1
Yields of crops on Sassafras loam
Mean weights in grams per pot

BORAX	RADISH		LETTUCE		OATS	SPINACH	
	Fresh Weight of Roots	Total Dry Weight of Roots and Tops	Fresh Weight of Tops	Dry Weight of Tops	Dry Weight as Hay	Fresh Weight of Tops	Dry Weight of Tops
<i>lbs./A.</i>							
0	21.60 \pm 0.66	4.10 \pm 0.14	102.00 \pm 3.35	10.17 \pm 0.18	20.50 \pm 0.44	32.20 \pm 0.88	4.27 \pm 0.02
10	23.10 \pm 2.17	4.30 \pm 0.23	104.30 \pm 5.15	10.83 \pm 0.40	20.80 \pm 0.24	28.30 \pm 0.92	4.03 \pm 0.13
20	22.70 \pm 1.76	4.28 \pm 0.10	89.30 \pm 4.06	8.17 \pm 0.13	21.30 \pm 0.56	29.70 \pm 0.94	4.60 \pm 0.14

a rotation of corn, oats, wheat, and 2 years of timothy has been used during the 30 years of continual experiments. In every case the crop has been removed.

In one group of pots containing this soil, Fordhook lima beans were grown with the following treatments of borax, 0, 2½, 5, 10, 20, and 40 pounds per acre. In another group of pots receiving the same treatments of borax, Keystone oats were planted. When the oats were removed the soil was planted to Scarlet Globe radishes, and the treatments of borax were repeated. All yields are given in table 2.

The results show that oats did not respond favorably even to the very small applications of borax, despite the fact that this soil had been cropped continuously for 30 years without any application of fertilizers. The yields of oats grown on untreated soil were at least equal to those of plants grown on borax-treated soils. The total dry weight of radish plants and beans, however, showed a significant beneficial response to an application of borax. Although the total dry weight of radishes was increased by an application of 2½ pounds

of borax and the total dry weight of beans increased by a 5-pound application, no further increases in yield were observed with the larger applications.

Toxicity of boron was observed on oats grown on soil with an application of 10 pounds of borax per acre. Such symptoms became increasingly severe as the amount of borax was increased. Beans showed slight toxicity with the 20-pound application of borax, and more severe symptoms were noted with the 40-pound application. The weights showed a marked reduction in yield with the 40-pound application. With radishes, slight toxicity symptoms appeared on plants grown with the 40-pound application of borax, but no decrease was noted in yield.

Collington sandy loam

A crop of Scarlet Globe radish, followed by a crop of Big Boston lettuce and later by Bountiful string beans, was grown in one group of pots. Treatments

TABLE 2
Yields of crops on Sassafras loam from plot 7B
Mean weights in grams per pot

BORAX	LIMA BEANS		OATS	RADISH		
	Fresh Weight of Beans	Dry Weight of Beans and Vines	Dry Weight of Hay	Fresh Weight of Roots	Fresh Weight of Tops	Dry Weight of Roots and Tops
<i>lb./A.</i>						
0	37.66 \pm 0.67	13.39 \pm 0.66	21.76 \pm 1.02	48.33 \pm 2.41	28.83 \pm 0.37	4.66 \pm 0.02
2.5	35.56 \pm 1.98	13.06 \pm 0.71	18.33 \pm 0.41	57.83 \pm 2.39	24.66 \pm 1.59	5.20 \pm 0.11
5.0	38.90 \pm 1.77	14.59 \pm 0.66	19.10 \pm 0.25	53.50 \pm 1.15	29.83 \pm 1.32	5.13 \pm 0.07
10.0	37.00 \pm 2.32	14.12 \pm 0.58	19.70 \pm 0.33	56.33 \pm 1.63	29.52 \pm 0.84	5.33 \pm 0.13
20.0	36.33 \pm 1.73	12.29 \pm 0.56	19.36 \pm 0.13	59.00 \pm 1.70	27.16 \pm 0.51	5.07 \pm 0.11
40.0	26.33 \pm 1.70	10.20 \pm 0.26	19.30 \pm 0.16	53.83 \pm 2.20	32.16 \pm 0.37	5.20 \pm 0.17

of 0, 10, and 20 pounds of borax were applied to both section A, containing the soil at the original pH of 5.90, and section B, containing the soil limed to a pH of 6.50. In another group of pots receiving similar borax treatments, a crop of Keystone oats was followed by a crop of Bloomsdale Long Standing spinach. The results are presented in table 3.

The results show that it was not necessary to add boron to this soil type for the crops grown. Toxicity symptoms were apparent on the 20-pound treatment with all crops.

Colts Neck loam

Lettuce and string beans were grown on one group of pots containing Colts Neck loam according to the plan followed with Collington sandy loam. Section A, with an original pH of 5.04, received no lime; section B was limed to a pH of 6.6. In another group of oats similarly treated, a crop of oats was followed by a crop of spinach. Results are given in table 4.

TABLE 3
Yields of crops on Collington sandy loam
Mean weights in grams per pot

BORAX lbs./A.	RADISH		LETTUCE		STRING BEANS		OATS		SPINACH	
	Fresh Weight of Roots	Total Dry Weight of Roots and Tops	Fresh Weight of Tops	Dry Weight of Tops	Fresh Weight of Beans	Dry Weight of Beans and Vines	Dry Weight as Hay	Fresh Weight of Tops	Dry Weight of Tops	
Section A, pH = 5.90										
0	13.76 ±0.56	4.40 ±0.06	103.70 ±6.41	9.40 ±0.35	27.66 ±1.70	13.40 ±0.90	19.00 ±0.15	28.50 ±0.16	2.93 ±0.05	
10	11.53 ±0.64	4.30 ±0.05	102.70 ±8.97	9.50 ±0.56	24.63 ±0.85	12.00 ±0.85	18.50 ±0.32	28.00 ±0.72	3.00 ±0.10	
20	11.66 ±0.99	4.30 ±0.06	113.80 ±4.03	9.90 ±0.27	22.20 ±1.70	11.39 ±0.30	17.30 ±0.35	26.50*	2.95*	
Section B, pH = 6.50										
0	21.66 ±1.20	3.96 ±0.02	150.00 ±6.99	13.30 ±0.37	22.76 ±1.65	11.43 ±0.97	17.30 ±0.33	28.66 ±0.48	3.96 ±0.08	
10	22.80 ±1.68	4.00 ±0.03	141.30 ±7.89	12.93 ±0.24	22.33 ±0.57	11.10 ±0.46	17.30 ±0.16	29.16 ±0.60	3.90 ±0.003	
20	18.33 ±0.78	3.90 ±0.06	139.80 ±6.78	13.40 ±0.20	20.10 ±0.51	10.60 ±0.52	16.60 ±0.24	31.83 ±0.88	4.06 ±0.10	

* Average of two samples.

TABLE 4
Yields of crops on Colts Neck loam
Mean weights in grams per pot

BORAX lbs./A.	RADISH		LETTUCE		STRING BEANS		OATS		SPINACH	
	Fresh Weight of Roots	Total Dry Weight of Roots and Tops	Fresh Weight of Tops	Dry Weight of Tops	Fresh Weight of Beans	Dry Weight of Beans and Vines	Dry Weight as Hay	Fresh Weight of Tops	Dry Weight of Tops	
Section A, pH = 5.04										
0	7.03 ± 0.28	2.13 ± 0.02	Crop failed to grow on this section			38.83 ± 1.72	15.03 ± 0.42	11.60 ± 0.27	25.50 ± 0.28	2.93 ± 0.05
10	7.33 ± 0.40	2.17 ± 0.05				34.63 ± 0.93	14.16 ± 0.37	12.10 ± 0.36	26.33 ± 1.15	2.83 ± 0.10
20	4.33 ± 0.09	2.07 ± 0.04				35.80 ± 0.77	14.80 ± 0.85	12.26 ± 0.21	24.83 ± 1.04	2.90 ± 0.11
Section B, pH = 6.60										
0	6.66 ± 0.09	2.20 ± 0.004	97.30 ± 4.32	9.66 ± 0.15	30.86 ± 0.63	12.73 ± 0.35	13.40 ± 0.35	28.13 ± 1.39	3.66 ± 0.08	
10	6.83 ± 0.24	2.10 ± 0.03	100.60 ± 6.56	9.40 ± 0.29	30.10 ± 0.66	10.86 ± 0.57	12.53 ± 0.32	31.00 ± 1.64	3.76 ± 0.15	
20	6.50 ± 0.16	2.06 ± 0.05	101.00 ± 9.56	9.90 ± 0.53	23.73 ± 0.47	9.86 ± 0.34	13.28 ± 0.23	24.50 ± 0.69	3.16 ± 0.10	

The results show that this soil type, like Sassafras loam and Collington sandy loam, required no addition of boron. As in the other soils, toxicity symptoms were quite apparent with the 20-pound borax treatment.

Sassafras sand

Since the original pH of the sample of Sassafras sand was 4.5, both sections were limed. Each pot in section A received the equivalent of 4000 pounds of lime per acre; and each pot in section B, the equivalent of 7000 pounds. This raised the pH of section A to 7.03 and that of section B to 7.66. Borax was applied to pots in each section as follows: 0, 2½, 5, 10, 20, and 40 pounds per

TABLE 5
Yields of radishes on Sassafras sand
Mean weights in grams per pot

BORAX <i>lbs./A.</i>	FRESH WEIGHT OF ROOTS	FRESH WEIGHT OF TOPS	DRY WEIGHT OF ROOTS AND TOPS
<i>Section A, pH = 7.03</i>			
0	12.66 ±1.01	26.53 ±1.14	3.23 ±0.14
2.5	33.66 ±2.38	25.73 ±0.47	4.56 ±0.13
5.0	35.96 ±1.24	24.20 ±0.28	4.53 ±0.18
10.0	31.33 ±1.56	22.96 ±0.64	3.73 ±0.43
20.0	17.83 ±1.71	20.40 ±0.75	2.90 ±0.14
40.0	6.43 ±0.12	14.60 ±0.72	1.83 ±0.02
<i>Section B, pH = 7.66</i>			
0	14.10 ±0.75	21.86 ±0.65	2.60 ±0.10
2.5	37.10 ±1.10	21.40 ±0.68	4.06 ±0.13
5.0	39.03 ±2.11	21.06 ±0.26	4.06 ±0.12
10.0	33.30 ±2.54	22.03 ±0.47	3.73 ±0.14
20.0	28.33 ±3.36	21.33 ±1.44	3.63 ±0.29
40.0	6.60 ±0.77	13.66 ±0.15	1.66 ±0.09

acre. Both sections were planted to Scarlet Globe radishes. Results are given in table 5.

The yield of radishes grown on Sassafras sand shows definitely the beneficial response of radishes to borax under certain conditions. This beneficial response was not evident in the weights of the leaves, but was quite evident in the weights of roots. The 2½-pound application of borax per acre increased the weight of roots, but further increases of borax did not markedly further increase the yield. In fact, mild signs of borax injury began to appear at the 20-pound application and became more severe with the 40-pound treatment. Practically identical results were noted in both sections.

Hagerstown silt loam

Experiment 1. Section A received no lime; each pot in section B received the equivalent of 2000 pounds of lime per acre. The following treatments were set up for each section: 0, 10, 20, and 40 pounds of borax per acre. All of the pots were planted to White Icicle radishes. The yields are shown in table 6.

Experiment 2. As soon as the radishes were harvested from both sections in experiment 1, an additional application of lime equivalent to 4000 pounds per acre was made to each of the pots of section B, raising the pH to 7.67. No lime was applied to section A. The borax and fertilizer treatments of

TABLE 6
Yields of radishes on Hagerstown silt loam
Mean weights in grams per pot

BORAX lbs./A.	EXPERIMENT 1			EXPERIMENT 2		
	Fresh Weight of Roots	Fresh Weight of Tops	Dry Weight of Roots and Tops	Fresh Weight of Roots	Fresh Weight of Tops	Dry Weight of Roots and Tops
	<i>Section A, pH = 5.91</i>			<i>Section A, pH = 5.82</i>		
0	28.30*	28.00*	5.10*	51.06 ±2.12	17.10 ±0.30	4.83 ±0.02
10	26.26 ±0.79	26.10 ±0.37	4.56 ±0.13	46.76 ±1.73	15.13 ±0.27	4.20 ±0.06
20	23.90 ±1.43	28.20 ±1.04	4.06 ±0.27	43.66 ±0.53	15.30 ±0.08	3.96 ±0.15
40	14.93 ±0.21	29.13 ±0.69	3.26 ±0.06	24.36 ±0.67	19.70 ±0.33	2.83 ±0.05
	<i>Section B, pH = 6.58</i>			<i>Section B, pH = 7.67</i>		
0	28.43 ±0.63	26.90 ±0.31	4.76 ±0.12	32.43 ±1.24	27.80 ±0.22	4.36 ±0.07
10	27.03 ±1.48	29.00 ±0.39	4.85 ±0.10	44.00 ±0.91	28.26 ±1.12	5.30 ±0.14
20	23.36 ±1.05	26.00 ±0.59	3.86 ±0.18	47.10 ±1.33	26.23 ±0.28	4.80 ±0.08
40	14.43 ±1.13	26.26 ±0.32	3.33 ±0.19	42.90 ±0.79	25.86 ±0.43	4.83 ±0.14

* Average of two samples.

experiment 1 were repeated, and all pots were replanted to White Icicle radishes. The results are given in table 6.

An analysis of the results of experiments 1 and 2 is extremely interesting. In the first experiment there was essentially no difference between plants grown on section A and section B. In both sections, plants grown on the untreated soil were the best. Slight toxicity was observed on plants in both sections when grown on soil receiving 40 pounds of borax per acre. In the second experiment, however, there was a clear-cut difference in response to borax, between the two sections. In this case, plants in section A showed no beneficial response to borax, and there were definite signs of toxicity with the 40-pound treatment and slight injury with the 20-pound treatment. In section B, plants grown on soil receiving no borax exhibited mild signs of boron deficiency. The leaves were small, and the roots were dull gray and showed cracking of the

epidermis. The 10-pound application of borax produced plants which were healthy in every respect. Plants grown with larger amounts of borax showed no marked increase over those with 10 pounds of borax. Another interesting observation was the fact that there were no signs of boron toxicity on any plants grown on section B. This fact supports the view that boron becomes less available at the higher pH levels.

Dunellen sandy loam

The original pH of Dunellen sandy loam was too low to grow satisfactory crops; therefore, section A, consisting of eighteen 2-gallon pots each containing 17 pounds of soil, was limed to a pH of 5.80 by an application of lime equivalent

TABLE 7
Yields of radishes on Dunellen sandy loam
Mean weights in grams per pot

BORAX <i>lbs./A.</i>	FRESH WEIGHT OF ROOTS	FRESH WEIGHT OF TOPS	DRY WEIGHT OF ROOTS AND TOPS
<i>Section A, pH = 5.80</i>			
0	87.50 \pm 2.52	45.16 \pm 2.54	12.90 \pm 0.08
2.5	76.83 \pm 3.22	49.00 \pm 0.66	12.50 \pm 0.25
5.0	75.33 \pm 3.40	51.66 \pm 0.39	12.70 \pm 0.01
10.0	87.88 \pm 2.16	48.50 \pm 1.59	13.30 \pm 0.23
20.0	75.33 \pm 2.80	48.66 \pm 1.79	12.53 \pm 0.37
40.0	50.83 \pm 5.93	42.83 \pm 2.54	10.40 \pm 0.77
<i>Section B, pH = 7.06</i>			
0	23.00 \pm 0.87	52.00 \pm 1.57	8.13 \pm 0.13
2.5	32.60 \pm 0.38	55.50 \pm 2.73	9.16 \pm 0.18
5.0	33.83 \pm 1.15	57.83 \pm 0.44	9.63 \pm 0.32
10.0	35.16 \pm 3.37	54.00 \pm 0.47	9.26 \pm 0.41
20.0	32.66 \pm 2.31	51.83 \pm 1.49	8.80 \pm 0.10
40.0	30.83 \pm 1.79	3.52 \pm 0.96	8.96 \pm 0.47

to 3000 pounds per acre. Section B, consisting of eighteen similar pots of soil, was limed to a pH of 7.06 by an application of 9000 pounds of lime per acre. The following treatments were set up in each section: 0, 2½, 5, 10, 20, and 40 pounds of borax per acre. All pots were planted to White Icicle radish. The results are given in table 7.

In section A, no beneficial response to borax was observed; there were definite signs of boron injury on plants grown with 40 pounds of borax per acre; and slight toxicity was observed with the 20-pound treatment. In section B there was a definite beneficial response to borax. The weights of roots were greatly increased by an application of 2½ pounds of borax per acre and were slightly further increased by an application of 5 pounds. The roots of plants in section

B receiving no borax were gray and rough. Although the yields on this section were better with borax than without borax, none of the yields were so good as those from section A.

Sassafras sandy loam

For section A, 12 pots were filled with Sassafras sandy loam without lime, and for section B, 12 corresponding pots were prepared and limed to a pH of

TABLE 8
Yields of radishes on Sassafras sandy loam
Mean weights in grams per pot

BORAX lbs./A.	FRESH WEIGHT OF ROOTS	FRESH WEIGHT OF TOPS	DRY WEIGHT OF ROOTS AND TOPS
<i>Section A, pH = 5.45</i>			
0	30.00 \pm 1.46	24.53 \pm 0.61	4.53 \pm 0.07
10	34.80 \pm 1.77	17.30 \pm 0.40	3.93 \pm 0.08
20	21.83 \pm 0.67	18.20 \pm 0.35	3.26 \pm 0.10
40	20.26 \pm 0.18	14.96 \pm 0.35	2.63 \pm 0.03
<i>Section B, pH = 7.16</i>			
0	23.36 \pm 2.35	17.73 \pm 1.33	3.30 \pm 0.27
10	28.80 \pm 1.78	19.56 \pm 0.60	3.90 \pm 0.16
20	31.46 \pm 0.45	13.96 \pm 0.33	3.40 \pm 0.05
40	26.66 \pm 1.41	15.53 \pm 0.77	3.30 \pm 0.04

TABLE 9
Boron content of plants as influenced by additions of borax to the soil

BORAX ADDITIONS TO SOIL lb./A.	BORON CONTENT OF PLANTS						
	Oats	Spinach	Beans		Lettuce	Radish	
			Vines	Pods		Tops	Roots
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0	6	23	24	12	28	29	13
10	22	80	28	12	37	89	19
20	50	105	60	13	60	204	34

7.16. The following borax treatments were applied in each section: 0, 10, 20, and 40 pounds per acre. All pots were planted to White Icicle radish. Results are given in table 8.

On this soil, as on Sassafras sand, Hagerstown silt loam, and Dunellen sandy loam, there was evidence that the borax in some manner had become less available at the higher pH level. In section A, plants grown without borax produced healthy roots, whereas plants receiving 40 pounds of borax per acre showed signs of injury. In section B, plants grown without any borax had

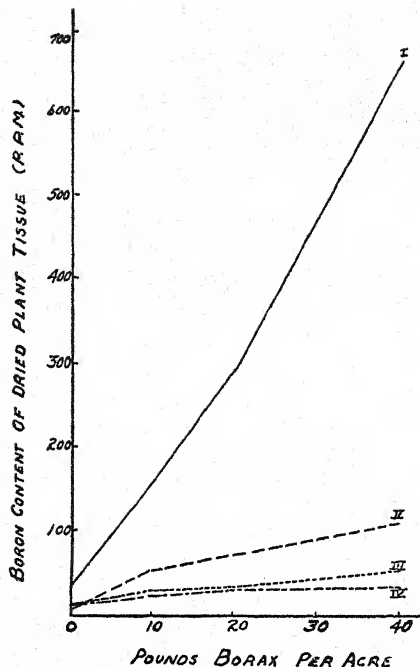


FIG. 1. BORON CONTENT OF RADISHES GROWN ON HAGERSTOWN SILT LOAM

Two applications of borax at the rate indicated, I, Leaves grown at pH 5.82; II, Leaves grown at pH 7.67; III, Roots grown at pH 5.82; IV, Roots grown at pH 7.67.

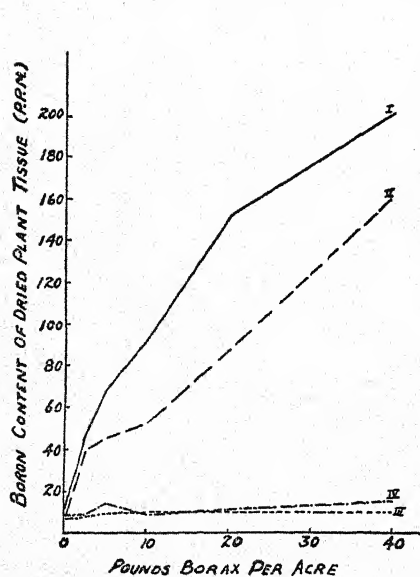


FIG. 2

FIG. 2. BORON CONTENT OF RADISHES GROWN ON DUNELLEN SANDY LOAM

I, Leaves grown at pH 5.80; II, Leaves grown at pH 7.06; III, Roots grown at pH 5.80; IV, Roots grown at pH 7.06.

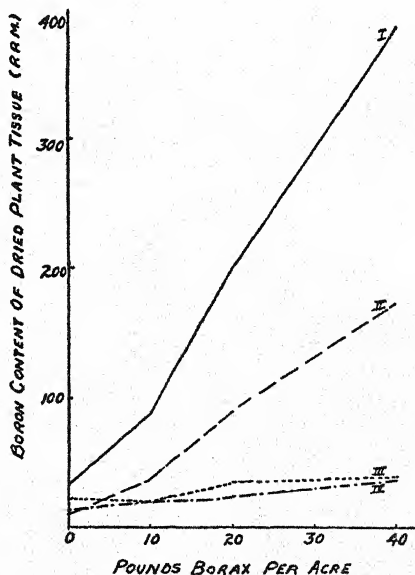


FIG. 3

FIG. 3. BORON CONTENT OF RADISHES GROWN ON SASSAFRAS SANDY LOAM

I, Leaves grown at pH 5.45; II, Leaves grown at pH 7.16; III, Roots grown at pH 5.45;

cracked, discolored roots; the plants receiving borax showed a small increase in size and were healthy in appearance. No plants in this section showed borax toxicity even with the 40-pound treatment.

ANALYSIS OF PLANTS FOR BORON

The results of the chemical analysis of plant materials, given in table 9, indicate that certain plants, at least, take up boron somewhat in proportion to the amount of available boron present. Evidently, this does not hold for roots of radishes or for the pods of beans, the amount of boron present varying only slightly regardless of whether the plant was grown in soil containing a small or a large amount of borax.

The effects of pH upon the availability of boron are clearly illustrated in figures 1, 2, and 3. The boron content of leaves of radish grown on Sassafras sandy loam and Hagerstown silt loam limed to a pH of about 7.2-7.7 was less than half the amount found in leaves of radish plants grown on these same soils at lower pH levels.

CONCLUSION AND DISCUSSION

Although this investigation is not complete, several interesting points are brought out.

The need for taking special care to provide additional boron in fertilizers is not a general problem for farmers working with soils similar to those used in this experiment.

Of all the soils tested at their original pH, only one (Sassafras loam from plot 7B) gave any beneficial response to applications of borax and then not for all crops grown on this soil. The response on this soil shows that it is possible to bring about mild boron deficiency in certain crops if the soil is continuously cropped and no boron supplied. Even when four of these soils (Colts Neck loam, Collington sandy loam, Dunellen sandy loam, and Hagerstown silt loam) were limed reasonably, they failed to give any beneficial response to borax. It was shown that all soils used, with the exception of Sassafras loam from plot 7B, were capable of producing good crops even though chemically pure salts were used as fertilizers and no borax was applied. At least several of these soils (Sassafras loam, Collington sandy loam, Colts Neck loam) were able to produce several crops with the use of fertilizers made from chemically pure salts, and with no additions of borax.

Although the application of boron is hardly a general necessity, it is possible under certain liming practices to bring about a condition which will be improved by applications of borax. Radish grown on all soils which had been limed to a pH somewhat above 7.0 showed an increase in root yield when borax was supplied. Plants grown on these soils at a high pH without borax developed mild boron deficiency symptoms. In no case were there any of the *marked* boron deficiency symptoms, such as death of the growing point of root and shoot, which have been noticed by observers working with sand and solution cultures.

The fact that a high pH is instrumental in making boron less available was clearly indicated by the *mildness* of the toxicity symptoms at the high pH levels studied. Boron toxicity on radish plants grown on these soils was for the most part very mild or absent even on plants grown on soil receiving 40 pounds of borax per acre. On the same soil at a lower pH, radish plants exhibited severe injury when grown with the 40 pounds per acre, and in some cases severe toxicity was apparent with the 20-pound application.

Chemical analysis of plant materials showed that the amount of boron in the plant is markedly increased as the amounts of borax added to the soil are increased. Roots of radish and pods of beans, however, are exceptions.

The analysis also proved that boron was made less available at the higher pH levels. In some cases the amount of boron in the plant grown at the high pH levels was less than half that in plants grown in the same soil at a lower pH and receiving the same amount of borax.

It must be remembered, however, that on most soils large amounts of lime were required to raise the pH high enough for crops to respond beneficially to borax. Such high pH values would be relatively rare in the soil types investigated. Also, in some cases 10 pounds of borax per acre was sufficient completely to rectify the boron deficiency, and in no case was there any extra beneficial response noted above the 20-pound treatment. As some fertilizers contain traces of boron (50, 41), it would not be advisable to apply more than 20 pounds of borax to the acre, even on soils limed to a high pH. Larger applications may injure sensitive plants.

SUMMARY

To determine whether the use of borax on certain soils would result in improved growth, crops were grown on eight different soils receiving fertilizers made from chemically pure salts and watered with distilled water.

Of the crops grown on six soils at their original pH values, only radishes and beans on Sassafras loam from plot 7B (nitrogen availability plots previously described) gave any beneficial response to borax.

Three soils, even when limed to a pH of 6.0–6.6, failed to give any beneficial response to borax.

Four soils, including one of those which had failed to give any beneficial responses when limed to a pH of 6.0–6.6, did give a beneficial response to applications of borax when limed to a pH > 7.0.

Applications of borax on soils limed to a high pH (pH > 7.0) markedly increased the root weight of radishes. In some cases a treatment of 2½ pounds of borax per acre corrected the deficiency, and in no case were benefits noted beyond the 20-pound treatment per acre.

Boron is made less available on soils limed to a pH above 7.0. Besides the effects on yields, this was clearly shown by the fact that a greater amount of borax was necessary to cause toxicity of plants grown on soils at a high pH.

The boron content of plants grown on soils having a pH > 7.0 is less than that of plants grown on the same soil at a lower pH.

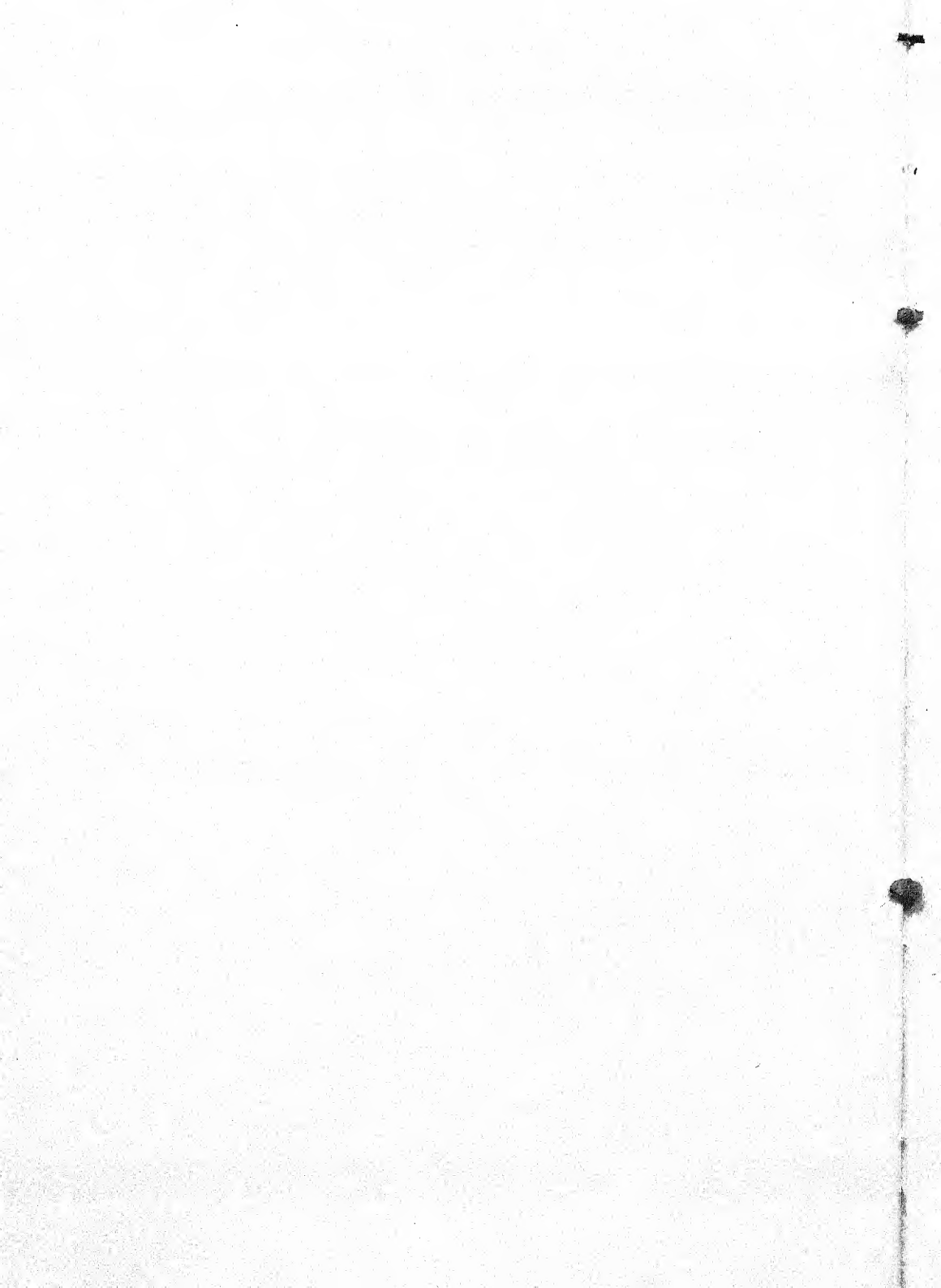
Plants grown on soils treated with borax show an increase in the boron content as the amount of borax applied to the soil is increased. Roots of radish and pods of beans, however, do not increase in boron content to any large extent as the borax concentration is increased in the soil.

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EFFECT OF APPLICATIONS OF MAGNESIUM ON CROP YIELDS AND ON THE PERCENTAGES OF CALCIUM AND MAGNESIUM OXIDES IN THE PLANT MATERIAL

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Magnesium is one of the elements essential for all crops. Until comparatively recently, however, it was assumed to be unnecessary to supply this element in the form of a commercial fertilizer, since, in general, normal soils contain a fair amount of magnesium and, further, because magnesium is supplied to many soils in the form of dolomitic limestone and in farm manure and may be present in small amounts in fertilizer materials.

MAGNESIUM IN NEW JERSEY SOILS

In general, the soils of New Jersey are fairly well supplied with magnesium (1, 2, 3). Soils like the Penn, Lansdale, Washington, Chester, Gloucester, Dutchess, Hagerstown, and Montalto in the northern part of the state commonly contain 1 per cent or more of MgO and, generally, a lower content of calcium. Of the Costal Plain soils, Collington and Keansburg are notably high in magnesium and in many places show higher percentages of magnesia than of lime. Lakewood and Sassafra sands are extremely low in both calcium and magnesium. Figure 1 indicates the relative amount of magnesia and figure 2 the relative amount of lime, in a few of the important soils of the state.

In recent years reports of magnesium deficiency in soils have come from several sections of the country, notably the potato sections of Maine and Virginia and certain tobacco sections in the South. Long-time experiments at this station with calcium and magnesium limestones have not indicated a definite magnesium deficiency in Sassafra loam which is being used for the growing of vegetables and general farm crops. Recently, however, yields of alfalfa and timothy from plots which have received magnesium limestone have been slightly better than yields from corresponding plots which have received calcium limestone, although no magnesium deficiency symptoms were apparent.³

¹ The authors wish to acknowledge their indebtedness to Arthur Grant, working under E.R.A. Project S-F2-101 and W.P.A. Project 4-1077, for a large part of the calcium and magnesium determinations on the plant materials, and to R. Straus for preparing the drawings for figures 4 and 5.

² The third author is now in soil work at Idaho Agricultural Experiment Station.

³ The calcium limestone used during the early part of the work (1908 to 1918) contained about 1.25 per cent of magnesia; that used more recently, about 5.0 per cent magnesia.

SYMPTOMS OF MAGNESIUM DEFICIENCY

Magnesium is a constituent of the green coloring matter of plants. In soils deficient or very low in this element, the plant may not make normal growth.

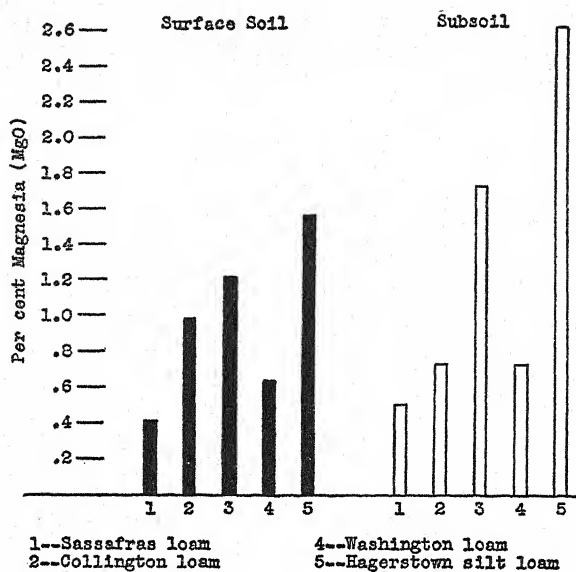


FIG. 1. PERCENTAGE OF MAGNESIUM OXIDE IN SOME LOAM SOILS OF NEW JERSEY

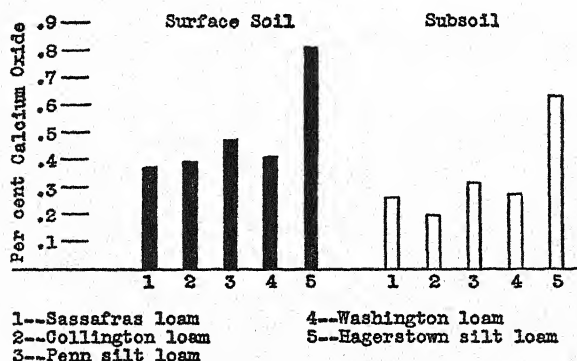


FIG. 2. PERCENTAGE OF CALCIUM OXIDE IN SOME LOAM SOILS OF NEW JERSEY

In describing magnesium deficiency symptoms in tobacco McMurtrey (11) says:

The specific symptom of magnesium hunger is the loss of the green color at the tip and margins of the lower leaves of the plant. This loss of color seems to advance toward the base of the individual leaf and may extend to the upper leaves of the plant depending upon

the acuteness of the deficiency. In some instances the entire lower leaves may be almost white when the trouble is first recognized, although the veins and mid-rib tend to retain their normal green color. The symptoms in the field are identical with those produced under controlled conditions.

Wallace (15) points out that the ratio of potassium to magnesium may be important in apple and raspberry growing in cases where manure is not procurable and the grower has to rely solely on the use of artificial manures, since magnesium deficiency results in very serious premature defoliation of these plants.

In their paper on the nutrition of apple trees, Blake, Nightingale, and Davidson (4) say:

When magnesium was withheld, a characteristic type of leaf injury soon developed and was followed by abscission of the affected leaves. The current stems of trees lacking magnesium were very low in carbohydrates, small in diameter, and deficient in woodiness.

In addition to using magnesium salts and dolomitic limestone in connection with the fertilizer treatment, Chucka (7) used magnesium as a spray on potato plants in Maine. Discussing the effects, he says:

In all cases marked response to added magnesium was noted in 5 to 10 days after the magnesium was added. The chlorotic leaves did not seem to regain their green color, but no more chlorosis developed on the old leaves after the addition of magnesium and all of the new growth had a healthy green appearance. In the fall the untreated plants died early while the treated plants remained green until killed by late blight or frost.

He also points out that the effect of the magnesium on yield of potatoes was surprisingly great.

Jacks and Scherbatoff (9) direct attention to the part which magnesium plays in the chlorophyll molecule and comment as follows:

Magnesium deficiency symptoms are probably the immediate result of an insufficiency of the element, and therefore of chlorophyll, in the plant, and the fact that the symptoms have been observed most frequently on light acid soils suggests that they are often related to a true magnesium deficiency in the soil, rather than to conditions rendering magnesium "unavailable." Magnesium is one of the most soluble and most weakly absorbed of the common exchangeable cations, and actual deficiencies in soils may be much more common than has yet been recognized.⁴

⁴ Evidence presented by Joffe, Kardos, and Mattson (Joffe, J. S., Kardos, L. T., and Mattson, S. 1935 The laws of soil colloidal behavior: XVII. Magnesium silicate—its base-exchange properties. *Soil Sci.* 40: 255-268), seems to indicate that magnesium is a strongly adsorbed cation and may be fixed in the soil possibly as magnesium silicates.

Prince and Toth (Prince, A. L., and Toth, S. J. 1937 Effects of long continued use of dolomitic limestone on certain chemical and colloidal properties of a Sassafras loam soil. Paper presented before Sec. 2, Soil Science Society of America, Chicago, Dec. 3, 1937), have shown that approximately 25 to 30 per cent of the total calcium in soils treated with dolomitic limestone was exchangeable by extraction with normal ammonium acetate, and that only 3 to 5 per cent of the total magnesium was exchangeable. They point out further that the amount of electro-dialyzable calcium was similar to that extracted with normal

EXPERIMENTAL

Frequent inquiries with reference to the magnesium requirement of different crops indicated a need for work along this line. A series of pot experiments was started, therefore, in the fall of 1934 and continued throughout the winter. Greenhouse experiments were again conducted during the winter of 1935 and 1936; and outside experiments in cylinders and wooden forms and, to a limited extent, in the field, during the summers of 1936 and 1937.

The following soil types were used in this work: Sassafras loam, silt loam, sand, and fine sandy loam; Portsmouth loam; Collington loam; Penn loam and silt loam; Chester loam; Dunellen loam; Wethersfield loam. The field crops grown were buckwheat, rape, barley, corn, soybeans, and mixed hay. The vegetable crops were spinach, cabbage, radishes, beets, carrots, garden peas, string beans, tomatoes, and peppers, but not all crops were grown on all types of soil. In all cases where the soil was distinctly acid, calcium carbonate was added to bring the pH near to the point suitable for the crop to be grown. Also in all cases a complete fertilizer was used.

During the 3-year period over which this work extended, a large volume of data was accumulated. Very much of the work was negative, that is, in a good many cases the magnesium treatment resulted in some increase in yield, but in even more cases there was no increase or a decrease in yield as compared with the check treatment. The depression in yield was not generally of sufficient magnitude, however, to cause symptoms of magnesium toxicity. On the other hand, definite symptoms of magnesium deficiency were detected in one instance, with string beans on Sassafras sand⁵ (plate 1).

Crop yields

In view of the somewhat negative results, it seems unwise to load this report with a large number of tables of weights of individual crops under the various treatments.⁶ Tables showing yields on a few types of soil are given. These are more or less typical of results obtained with other crops and on other types of soil.

From a study of table 1, it is quite evident that the use of magnesium in pot experiments did not result in distinctly increased yields in very many cases. For soybeans and barley such increases as are noted are negligible. Carrots on Penn loam and Chester loam show increases with magnesium sulfate, but the same crop on Sassafras loam shows a decided decrease. String beans grown on Sassafras sand gave a distinct increase in yield with magnesium sulfate. In general, the use of the magnesium sulfate for vegetable crops resulted in about as many slight decreases in yield as increases. This does not neces-

ammonium acetate but that the value for electrodialyzable magnesium was only about 60 per cent of that obtained by the salt extraction method. They say, "The partial fixation of magnesium by silicates no doubt accounts for its incomplete removal by electrodialysis."

⁵ This soil is very low in mineral nutrients.

⁶ All the data are on file in the soil department and are available should they be called for.

sarily mean that the magnesium sulfate actually had a depressing effect but rather points to a negative effect as compared with the check treatment.⁷

In a further study of the influence of magnesium on crop yields, peppers were grown in 1935 and corn (as forage) was grown in 1936 on five types of soil. The soils (Portsmouth loam, Penn loam, Sassafras silt loam, Sassafras loam, and Sassafras sand) were placed in wooden forms 1 yard square with a soil depth of about 10 inches. For both peppers and corn two squares were left without magnesium, two were treated with magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) at the rate of 100 pounds to the acre, and two at the rate of 200 pounds. A

TABLE 1

Influence of magnesium on the yields of soybean hay, barley, spinach, carrots, and beets grown on different types of soils in pots

SOIL TYPE	MAGNESIUM TREATMENT	DRY WEIGHT		AS MARKETED		
		Soybean hay	Barley—grain and straw	Spinach	Carrots	Beets
		gm.	gm.	gm.	gm.	gm.
Sassafras loam	No magnesium	21.5	45.0	122	76	42
	2 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	23.2	45.7	84	46	39
	4 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	21.2	47.0	96	52	45
Penn silt loam	No magnesium	19.2	48.3	68	24	28
	2 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	20.0	47.7	69	44	39
	4 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	20.7	49.7	58	48	32
Chester loam	No magnesium	14.8	35.7	44	21	27
	2 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	13.3	37.3	48	25	29
	4 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	15.3	35.8	44	28	36
Dunellen loam	No magnesium	41.3	36
	2 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	43.3	35
	4 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	40.7	26
Wethersfield loam	No magnesium	10.0	37.3	32	...	23
	2 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	9.7	37.7	34	...	32
	4 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	9.7	36.7	32	...	29

4-8-6 fertilizer was used at the rate of 1000 pounds an acre, but only half was applied at the time of planting, the remaining half being applied July 16. For the corn in 1936 the magnesium application was increased to make it equivalent to 150 and 300 pounds to the acre. The fertilizer treatment was

⁷ In connection with fertilizer experiments with potatoes in several localities in the state, the department of plant pathology has used magnesium in the form of the sulfate and also as Kieserite and as dolomitic limestone. On two farms there was a fair response to the magnesium treatments for two successive years. Aside from these two farms, no appreciable increase in yield has been noted.

the same as that for the peppers in 1935, except that half the amount was broadcast before planting and the remainder used as two separate side-dressings. The green weight of peppers and the dry weight of corn forage are shown in table 2. The figures show that the magnesium-treated soil did not give a pronounced increase in yield of either peppers or corn except on Sassafras sand, which is one of the poorest soils in the state and has a very low content of both calcium and magnesium.

In 1937 cabbage was grown on the five types of soil in these forms, with a continuation of the magnesium treatment. The crop was a failure on Sassafras sand, no marketable heads being produced. On Penn loam, Sassafras

TABLE 2
Influence of magnesium on the yields of green pepper and corn forage grown in wooden forms 3 feet square

SOIL TYPE	MAGNESIUM TREATMENT, ACRE BASIS	GREEN WEIGHT OF PEPPERS	DRY CORN FORAGE
		gm.	gm.
Portsmouth loam	No magnesium	1,855	1,286
	100 lbs. $MgSO_4 \cdot 7H_2O$	1,845	1,162
	200 lbs. $MgSO_4 \cdot 7H_2O$	2,026	1,060
Penn loam	No magnesium	2,384	793
	100 lbs. $MgSO_4 \cdot 7H_2O$	2,032	724
	200 lbs. $MgSO_4 \cdot 7H_2O$	1,417	756
Sassafras silt loam	No magnesium	2,545	849
	100 lbs. $MgSO_4 \cdot 7H_2O$	2,396	872
	200 lbs. $MgSO_4 \cdot 7H_2O$	2,184	905
Sassafras loam	No magnesium	2,482	882
	100 lbs. $MgSO_4 \cdot 7H_2O$	1,999	727
	200 lbs. $MgSO_4 \cdot 7H_2O$	2,555	776
Sassafras sand	No magnesium	1,131	486
	100 lbs. $MgSO_4 \cdot 7H_2O$	1,344	533
	200 lbs. $MgSO_4 \cdot 7H_2O$	1,317	595

silt loam, and Sassafras loam, the magnesium treatment gave no significant increases in yield over those without magnesium. On Portsmouth loam, the average yield was 1480 gm. of marketable heads per square (9 square feet) without magnesium treatment; the average yield was 2178 gm. per square for the four squares that received magnesium sulfate; but the yield with the double portion of magnesium sulfate was somewhat smaller than with the single portion.

In another experiment, tomatoes were grown on three types of soil (Sassafras loam, Sassafras sand, and Collington loam) placed in wooden forms having a surface area of 4 square feet. The soil in the forms had a depth of

about 10 inches. Three squares for each type of soil received no magnesium and three received the magnesium sulfate at the rate of approximately 600 pounds an acre. A 4-8-6 fertilizer was used at the rate of 1000 pounds an acre, one-half applied at the time of setting plants and one-half later. The magnesium treatments and the yields of tomatoes are indicated in table 3. From the table it will be seen that with each type of soil there was an increase in yield of tomatoes where magnesium sulfate was applied, the increase amounting to 16 per cent for Sassafras loam, 19 per cent for Sassafras sand, and 25 per cent for Collington loam.

In 1936 string beans were grown in three types of soil (Sassafras loam, Collington loam, and Sassafras sand) placed in wooden forms 2 feet square. A complete fertilizer was used at the rate of 1000 pounds to the acre. To three squares representing each type of soil no magnesium was applied and to three other squares for each type, magnesium sulfate was applied at the rate of 600 pounds an acre. With Sassafras loam and Collington loam the magnesium

TABLE 3

Influence of magnesium on the yield of tomatoes grown in wooden forms 2 feet square

SOIL TYPE	MAGNESIUM TREATMENT	RIPE FRUIT
		gm.
Collington loam	No magnesium	7,392
	25 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	9,261
Sassafras loam	No magnesium	5,637
	25 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	6,521
Sassafras sand	No magnesium	2,580
	25 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	3,076

treatment had little effect on the yield. With Sassafras sand (very low in CaO and MgO) the three squares without magnesium gave a yield of 42 gm. of beans and 40 gm. of vines. The three squares with the magnesium treatment gave a yield of 64 gm. of beans and 116 gm. of vines. Plate 1 shows representative plants grown with and without magnesium.

Table 4 shows results obtained with mixed hay and with soybean hay, grown with different amounts of calcium and magnesium limestone on Sassafras loam in 1935 and 1936 respectively. The plots were 1/20 acre in size and had been under the limestone treatment since 1908, the applications being made at 5-year intervals up to 1928. Since that date no limestone has been applied. A moderate application of a complete fertilizer was made annually. Without exception, the yields with the magnesium limestone, as shown in table 4, are slightly higher than the yields with the calcium limestone. In six cases out of nine, however, the advantage of the magnesium limestone over the calcium limestone is less than 300 pounds of hay to the acre. In general

the pH of the soil on which the magnesium limestone is used is slightly higher than that of the soil on which the calcium limestone is used. This may account, in part, for the higher yields with the magnesium limestone.⁸

No general rule can yet be laid down for the use of magnesium, but where growers suspect magnesium deficiency it is safe to substitute dolomitic lime or limestone for calcium lime at intervals, as a matter of precaution. There need be no fear of injury from the judicious use of the dolomitic forms of lime. Where magnesium deficiency symptoms are detected, magnesium may be supplied in the form of the sulfate, dolomitic hydrate, or dolomitic limestone.

TABLE 4
*Influence of magnesium on the yields of mixed grasses and of soybean hay grown on
Sassafras loam in the field*
Treatments and yields on acre basis

LIME TREATMENT	PLOT NUMBER	YIELD OF MIXED GRASS HAY	PLOT NUMBER	YIELD OF SOYBEAN HAY, SECTION 1	PLOT NUMBER	YIELD OF SOYBEAN HAY, SECTION 2
		lbs.		lbs.		lbs.
No lime.....	35	2,100	21	1,486	28	1,575
1,000 lbs. Calcium limestone.....	36	2,588	22	2,450	29	2,275
2,000 lbs. Calcium limestone.....	37	3,290	23	2,885	30	3,239
4,000 lbs. Calcium limestone.....	38	3,924	24	3,534	31	3,648
1,000 lbs. Magnesium limestone*.....	39	2,871	25	2,643	32	2,706
2,000 lbs. Magnesium limestone.....	40	3,819	26	3,569	33	3,547
4,000 lbs. Magnesium limestone.....	41	4,077	27	3,763	34	3,782

* About 30 per cent magnesia (MgO) and 20 per cent lime (CaO).

Lime and magnesia in the crops

In the course of the work it was observed that in the majority of cases the percentage of MgO in the plant material increased with the increase in the amount of magnesium applied. It was noted also that there was a tendency for the CaO to decrease as the MgO increased.

Other investigators have pointed out that application of magnesium compounds has increased the magnesium content of the plant. In connection with magnesium deficiency studies in vegetable production, Carolus and Brown (6) have pointed out that fruits (peppers, tomatoes, and eggplants) from magnesium-fertilized plants, contained 42 per cent more MgO than those from unfertilized areas, and Carolus (5) has shown a higher percentage of magnesium in potato plants grown with hydrated magnesium lime and dolomitic limestone than with calcium lime or no lime.

⁸ A pound of pure magnesium carbonate, $MgCO_3$, has a slightly greater corrective effect than a pound of pure calcium carbonate.

Naftel (12) made a study of the effect of pure CaCO_3 and calcium-magnesium carbonate on the mineral content of sorghum grown on three types of soil. In each case the calcium-magnesium carbonate gave an increase in the percentage of magnesium in the plant material and a decrease in the percentage of calcium, as compared with the CaCO_3 -treated plants.

Cunningham (8) found that applications of magnesium sulfate to pastures slightly increased the percentage of MgO in the dry matter.

TABLE 5
*Influence of magnesium on the percentages of CaO and MgO in spinach
grown on different types of soils*

Dry matter basis

MAGNESIUM TREATMENT	PENN SILT LOAM		CHESTER LOAM		WETHERS-FIELD LOAM		SASSAFRAS LOAM NO. 1		SASSAFRAS LOAM NO. 2		SASSAFRAS FINE SANDY LOAM	
	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
No magnesium.....	2.19	1.45	1.75	2.97	2.01	0.84	2.22	0.97	1.75	1.23	3.52	1.05
2 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	2.04	2.04	1.89	3.28	1.78	1.53	1.84	1.93	1.64	1.53	3.00	2.02
4 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1.68	2.39	1.56	3.51	1.71	1.85	1.67	2.03	1.50	1.91	2.42	2.56

TABLE 6
*Influence of magnesium on the percentages of CaO and MgO in carrots grown on
different types of soils*

Dry matter basis

MAGNESIUM TREATMENT	SASSAFRAS LOAM				PENN SILT LOAM				CHESTER LOAM			
	Roots		Tops		Roots		Tops		Roots		Tops	
	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
No magnesium.....	.33	.23	2.47	.63	.43	.27	2.46	.60	.49	.29	2.95	.78
2 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$37	.26	2.25	.84	.38	.27	2.86	.63	.47	.30	2.77	.88
4 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$35	.32	2.19	.85	.35	.29	2.57	.69	.44	.29	2.79	.94

Lutman and Walbridge (10) note that Japanese millet plants grown with a minimum of magnesium contained about 25 per cent as much magnesium as similar plants grown in a solution carrying an abundance of this element. Scharrer and Schropp (13) say, "Applications of magnesium salts increased the magnesium content of the produce but were accompanied by a decrease in the calcium content."

Sherman (14, p. 240) reports inorganic elements in 150 American dietaries, and these indicate a little more than twice as much magnesium as calcium per 3000 calories.

Wherry (16) reports analyses of six species of plants growing in serpentine

barrens and in nearby Piedmont or Coastal Plain woods. He found when any species invades the magnesian soil of the barrens, there was a marked increase in the MgO content of its ash, although accompanying changes in other constituents show no regularity.

Among the vegetable crops analyzed for CaO and MgO were string beans, garden peas, carrots, beets, radishes, peppers, spinach, and cabbage. Other crops were barley, buckwheat, and soybeans for hay.

TABLE 7

Influence of magnesium on the percentages of CaO and MgO in string beans and cabbage plants grown on different types of soils

Dry matter basis

MAGNESIUM TREATMENT	STRING BEANS ON												CABBAGE PLANTS ON SASSAFRAS FINE SANDY LOAM	
	Sassafras loam				Penn silt loam				Chester loam					
	Beans		Vines		Beans		Vines		Beans		Vines			
	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
No magnesium	1.05	.42	3.93	0.65	1.28	.52	2.07	.51	.95	.51	3.65	.69	2.80	.36
2 gm. MgSO ₄ ·7H ₂ O.	1.18	.52	3.96	0.95	1.00	.50	4.13	.70	.98	.53	3.37	.92	2.61	.50
4 gm. MgSO ₄ ·7H ₂ O.	1.02	.56	3.76	1.20	0.95	.53	3.99	.78	.92	.57	3.45	.91	2.53	.64

TABLE 8

Influence of magnesium on the percentages of CaO and MgO in radishes grown on different types of soils

Dry Matter Basis

MAGNESIUM TREATMENT	SASSAFRAS LOAM				CHESTER LOAM				DUNELLEN LOAM				WETHERSFIELD LOAM			
	Roots		Tops		Roots		Tops		Roots		Tops		Roots		Tops	
	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
No magnesium	1.26	.36	7.02	.57	1.41	.53	6.92	0.74	1.48	.36	6.28	.28	1.33	.41	6.26	.41
2 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1.34	.41	6.90	.55	1.50	.64	6.93	0.79	1.36	.46	5.88	.52	1.18	.41	6.38	.53
4 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1.29	.48	6.68	.77	1.28	.61	7.17	1.01	1.13	.45	6.02	.58	1.20	.47	5.84	.58

Table 5 shows the percentage of CaO and MgO in spinach grown on several types of soil. It will be observed that in nearly every case the percentage of MgO in the plant material is increased with addition of magnesium sulfate. Spinach grown on Sassafras fine sandy loam which received 4 gm. of magnesium sulfate contained nearly two and a half times as much MgO as that grown without magnesium treatment. As was mentioned previously, the percentage of lime decreases as the percentage of magnesia increases. The spinach showed

only slight exception to this for all the types of soil. The type of soil also influences the percentage of magnesium in the plant. For example, on Chester loam without magnesium treatment, the percentage of MgO is 2.97, whereas with the 2- and 4-gm. treatments of magnesium sulfate, the percentages are 3.28 and 3.51 respectively.

Carrots (table 6) show a rather low percentage of CaO in the roots and a high percentage in the tops. The magnesium treatment generally resulted in some increase in the percentage of magnesium in the plant material. In this

TABLE 9

Influence of magnesium on the percentages of CaO and MgO in tomatoes grown on different types of soils

Dry matter basis

MAGNESIUM TREATMENT	SASSAFRAS LOAM				SASSAFRAS SAND				COLLINGTON LOAM			
	Fruit		Vines		Fruit		Vines		Fruit		Vines	
	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
No magnesium155	.358	3.09	.45	.131	.253	2.46	.41	.149	.331	2.89	.59
25 gm. MgSO ₄ ·7H ₂ O	.136	.315	2.80	.70	.231	.356	2.37	.59	.159	.244	2.91	.63

TABLE 10

Influence of magnesium on the percentages of CaO and MgO in rape and soybean grown on different types of soils

Dry matter basis

MAGNESIUM TREATMENT	RAPE GROWN ON						SOY BEAN HAY GROWN ON					
	Sassafras loam		Sassafras fine sandy loam		Sassafras loam		Penn silt loam		Chester loam		Wethersfield loam	
	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO	MgO
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
No magnesium	2.32	.39	3.20	.34	2.00	.63	2.02	.72	1.94	.73	1.97	.66
2 gm. MgSO ₄ ·7H ₂ O . . .	2.18	.45	3.10	.51	2.01	.73	2.00	.76	1.82	.75	2.20	.73
4 gm. MgSO ₄ ·7H ₂ O . . .	2.27	.54	2.95	.68	1.91	.79	1.93	.81	1.86	.82	2.04	.77

case the type of soil has not greatly influenced the percentage of CaO or MgO.

String beans (table 7) show approximately 1 per cent of CaO and about one-half per cent MgO. The vines are exceptionally high in CaO, some of the sample showing about 4 per cent. The percentage of CaO is high in young cabbage plants (table 7); it decreases with the magnesium treatment, whereas the magnesium increases.

The percentage of CaO in radishes (table 8) does not differ greatly for the different types of soil, the range being from about 1.2 to 1.4 per cent. The

percentage of CaO in the tops is very high, usually above 6 per cent. The magnesium in the plant material tends to increase as the application of magnesium sulfate is increased.

Tomatoes (table 9) show a low percentage of both CaO and MgO in the ripe fruit. The percentage of CaO in the vines is high, varying from about 2.5 to 3 per cent. The magnesium treatment influences the percentage of MgO in the vines more than in the fruit.

Rape and soybeans (table 10) show a rather high percentage of CaO, the highest percentage being noted in rape grown on Sassafras fine sandy loam.

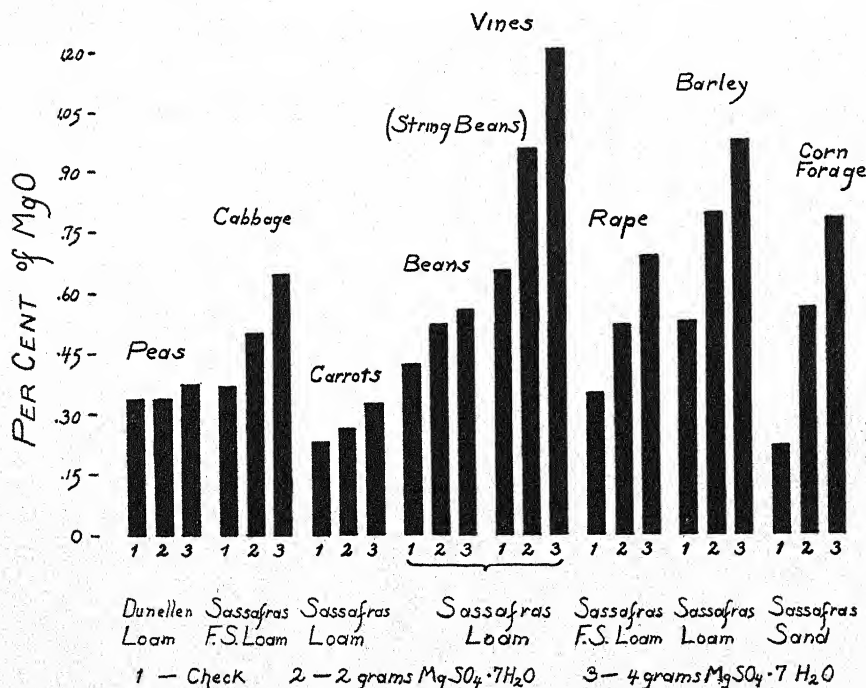


FIG. 3. PERCENTAGE OF MAGNESIUM OXIDE IN SEVERAL CROPS GROWN ON DIFFERENT TYPES OF SOIL, WITH AND WITHOUT MAGNESIUM TREATMENT

Without exception, the percentage of magnesium in the plant material increases with the addition of magnesium sulfate. The percentage of CaO and MgO in barley is low.

Figures 3 to 5 indicate graphically the variations in the percentages of CaO and MgO in the plant material, due to magnesium treatment.

Without undertaking to discuss the significance of increasing the magnesium content of the plant, we may point out that Lutman and Walbridge (10) in their exhaustive study of the role of magnesium in the aging of plants conclude: "... magnesium probably plays a secondary part in the senescence of plants.

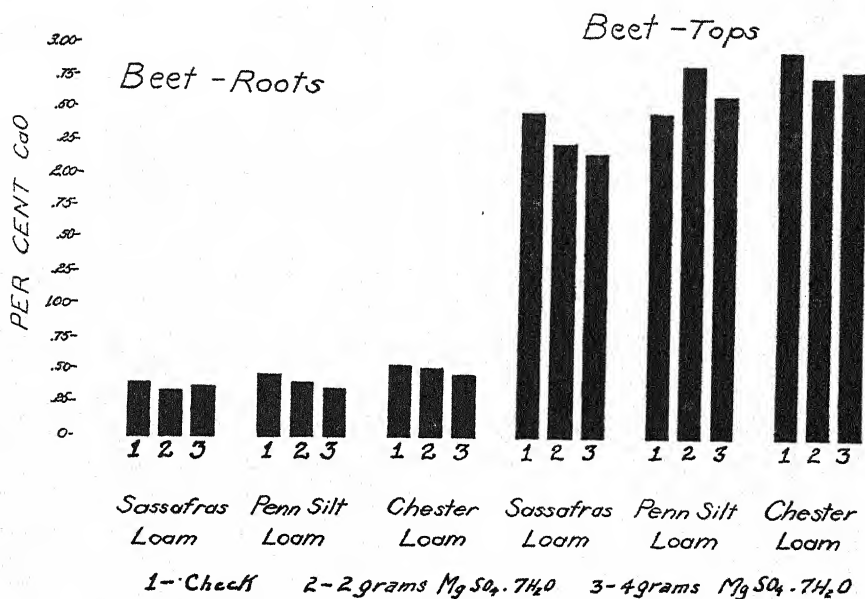


FIG. 4. PERCENTAGE OF CALCIUM OXIDE IN BEETS AND BEET TOPS GROWN ON THREE TYPES OF SOIL, WITH AND WITHOUT MAGNESIUM TREATMENT

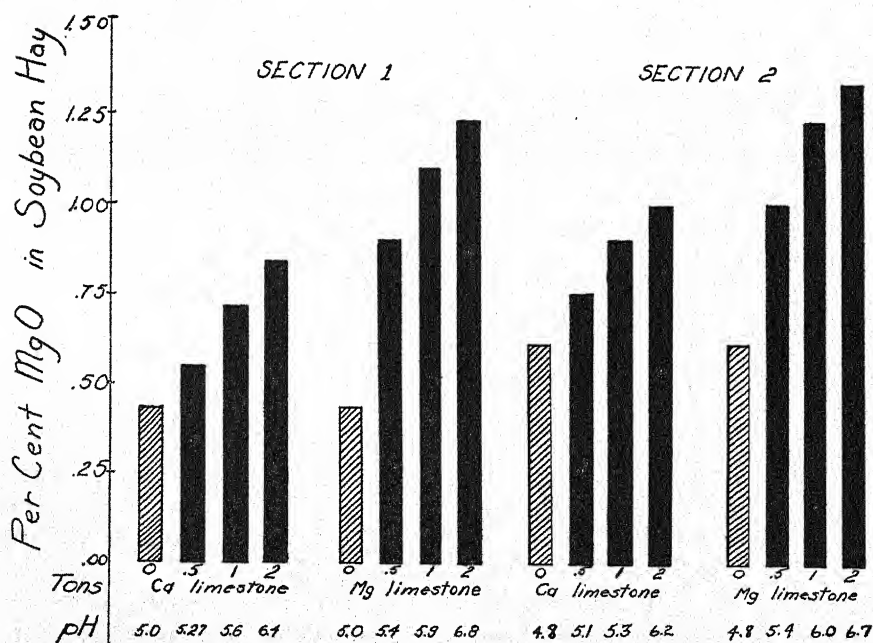


FIG. 5. PERCENTAGE OF MAGNESIUM OXIDE IN SOYBEAN HAY GROWN ON SASSAFRAS LOAM WITH DIFFERENT LIME TREATMENTS

Its lack may be one of the factors concerned therein, but probably many other and more complicated internal disturbances and rearrangements are responsible for all the phenomena associated with normal aging in plants."

Whether or not any importance is to be attached to the fact that the magnesium content of plants may be increased by the use of magnesium sulfate and other magnesium compounds, it is important to remember that the use of magnesium compounds in connection with fertilizer treatment may result in rather wide differences in the magnesium content of the plant. The type of soil, likewise, may be responsible for differences in the CaO and MgO content of the plant. It follows, therefore, that in reporting analyses, it is important, where possible, to state the conditions under which the plants were grown.

SUMMARY

Numerous analyses have shown that the soils of New Jersey, with the exception of some of the very sandy areas, contain a rather high percentage of magnesium. Chemical analysis, however, does not answer the question as to whether there may be considerable areas of farm land in the state where the supply of available magnesium is not enough for normal crop growth. Work was started, therefore, about three years ago for the purpose of gaining further information along this line.

A variety of vegetable crops, mixed hay, soybean hay, and corn forage were grown on several types of soil without magnesium treatment and also with magnesium sulfate or dolomitic limestone treatment. A part of the work was done in the greenhouse, a part in small wooden forms outside, and a part in the field.

Some of the vegetable crops gave definite increases in yield when magnesium sulfate was used. With a number of the crops the increases were negligible. In all the experiments, there were probably about as many decreases in yield as there were increases where magnesium sulfate was used. In one instance the decrease was sufficient to indicate magnesium deficiency. Such decreases as are noted more likely represent negative results or are incidental.

Tomatoes grown on Sassafras sand and on Sassafras and Collington loam gave definite increases when magnesium sulfate was used. String beans and corn forage grown on Sassafras sand gave fair increases with the magnesium sulfate treatment.

Mixed hay and soybean hay grown on field plots (Sassafras loam) where dolomitic limestone has been used over a long period, showed moderate increases when compared with yields from corresponding plots treated with calcium limestone (the calcium limestone, however, contained a small percentage of magnesium).

There is very little indication that the soils of northern New Jersey in general are deficient in magnesium for the crops to be grown. The work reported here gives some indication that certain of the soils of southern New Jersey may be deficient in magnesium for some crops.

Analysis of the plant material for CaO and MgO has shown very definitely that with applications of magnesium sulfate, the magnesium content of the plant is commonly increased to a point considerably above that of plants grown under similar conditions but without applications of magnesium. In some cases the increase was more than 100 per cent.

In a number of the crops, the CaO tends to decrease as the MgO increases.

Attention is directed to the fact that when studies are being made on the composition of plant material, it is important to know the type of soil and the fertilizer and liming practices followed in the growing of the crop.

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PLATE 1. STRING BEANS GROWN IN SASSAFRAS SAND

Left, with magnesium sulfate; right, without magnesium sulfate. Note the rough, abnormal appearance of the leaves, the slender stem, and the scarcity of nodules on the plant without magnesium.



PLATE 1

STUDIES IN THE ELECTRODIALYSIS OF SOILS: V. BACK TITRATION CURVES OF SOILS AND HUMATES

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Titration curves of soils are easily determined by shaking known weights of the base-free soils with increasing amounts of alkali for 48 hours and finding the pH values.¹ Back titration curves could be determined by adding increasing amounts of acid to known weights of fully saturated soil, but this procedure involves the accumulation of increasing amounts of a soluble salt which is bound to affect the reaction.² Electrodialysis, on the other hand, appears to be free from this objection, and therefore the base could be gradually removed and the pH value determined at every step. If such a procedure proved feasible, electrodialysis would be a much more useful method of study than any hitherto available for this purpose. The object of this investigation was to explore these possibilities.

EXPERIMENTAL

The application of the rotating anode to the electrodialysis of soils has already been described.³ In the apparatus devised for the purpose, the principle of electrofiltration was applied, and the electrodialyzate was continuously removed and collected. This apparatus proved satisfactory for soils but was slightly modified for humates (fig. 1). Parchment paper was supported on hardened filter paper (Whatman 50), since the latter, alone, allows ready passage of humates, but, as a support, ensures against leakage of humus through pinholes which sometimes develop in parchment papers. Good filter paper impregnated with collodion was found as satisfactory as parchment paper. The glass vessel in which the electrodialyzate was collected was an ordinary Erlenmeyer flask with the bottom knocked off. The dialyzate was collected at definite intervals by opening the stopcock and was replaced by fresh water. Current was taken from a 220-volt main and kept exactly at 0.1 ampere through a suitable resistance. The temperature did not rise above 32°C.

¹ Puri, A. N., and Asghar, A. G. 1938 Influence of salts and soil-water ratio on pH value of soils. *Soil Sci.* 46: 249-258.

² Puri, A. N., and Asghar, A. G. 1938 Titration curves and dissociation constants of soil acidoids. *Soil Sci.* 45: 359-367.

³ Puri, A. N., and Hoon, R. C. 1937 Studies in the electrodialysis of soils: I. Electrodialysis by the Rotating electrode. *Soil Sci.* 43: 305-309.

Electrodialysis of soils

The single-base soils used in this study were prepared from a black cotton soil of high base-exchange capacity. This soil contained about 5 per cent humus, which was destroyed by alkaline permanganate. As humus has been studied separately in this paper, this procedure was considered necessary to get a clear idea as to the behavior of each. After the destruction of humus, the soil was acid-treated and neutralized with different bases. All pH values were determined with the glass electrode. Na-soil was prepared by neutralizing the H-soil to different pH values, and the back titration curves were

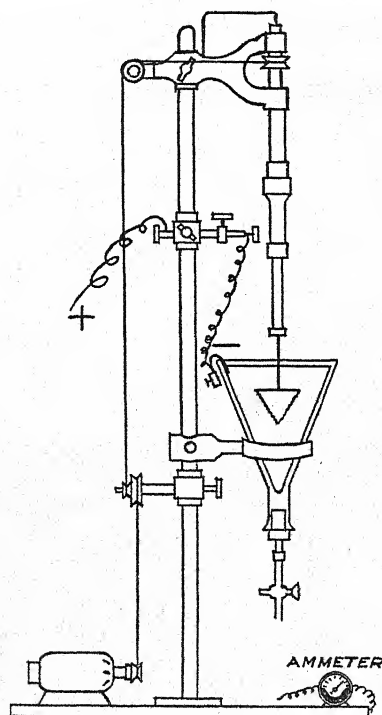


FIG. 1. APPARATUS USED FOR THE ELECTRODIALYSIS OF HUMATES

determined in every instance. In the case of other bases, only the highest pH value was taken. Five grams of each soil was used for electrodialysis. The results are plotted in figure 2 along with the forward titration curves of the H-soil. The remarkable difference in the forward and back titration curve is difficult to explain. It is seen that whatever the initial pH of the Na-soil, it falls rapidly to approximately that of the H-soil even when only 50 per cent of the base has been removed by electrodialysis. Further removal of the base produces but little effect on the pH value. This behavior is shown in a more striking manner where divalent bases are involved, especially with

Mg-soil, in which the pH drops to the lowest value when hardly 40 per cent of the base is removed by electrodialysis.

Electrodialyzed soil has frequently formed the material of study by various workers when a completely unsaturated or H-soil was required. The ultimate pH value or the reaction of the electrodialyzed soil has also acquired a certain amount of physical significance in soil literature. These results seem to show that unless electrodialysis is carried on for a very long time and proper care

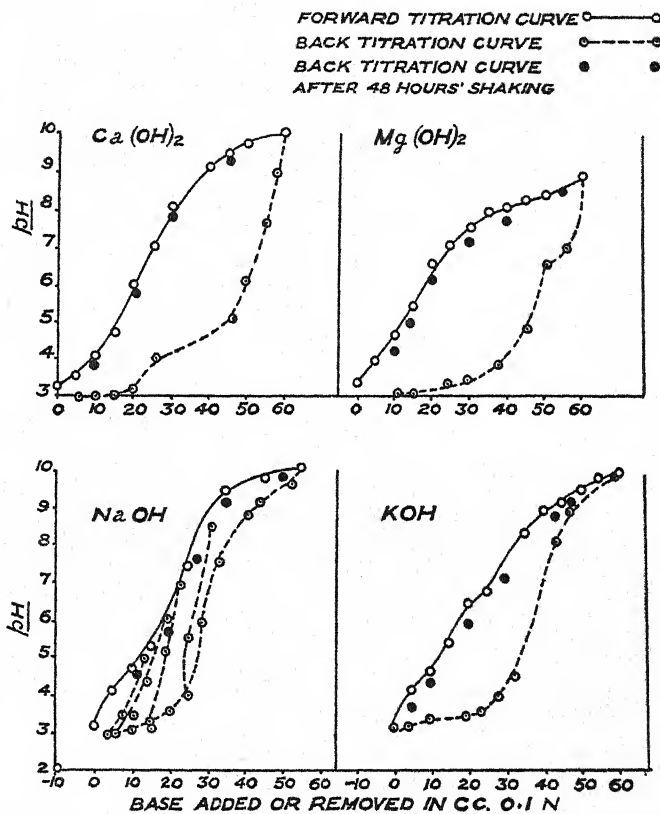


FIG. 2. FORWARD AND BACK TITRATION CURVES OF SOILS

is taken to watch the course of the reaction, this method of preparing unsaturated soils may easily lead to erroneous conclusions. Dilute-acid treatment for producing base-free soils, which has been adopted throughout these studies, is not only quicker but more reliable.

The enormous difference in the forward and back titration curves was baffling until the following reasoning was applied: when alkali is shaken with soil, at least 48 hours is required for attainment of equilibrium; therefore, if alkali is removed from the soil, an equally long time must elapse before

equilibrium can be established. The soil suspension was, therefore, shaken for 48 hours after each incremental removal of alkali, and the pH value was determined after shaking. The back titration curve thus obtained very nearly coincides with the forward curve.

The mechanism of pH changes in the soil due to the addition or removal of alkali may be visualized somewhat as follows: The complex ferroalumino-silicates which are mainly responsible for the acidoid character of the clay

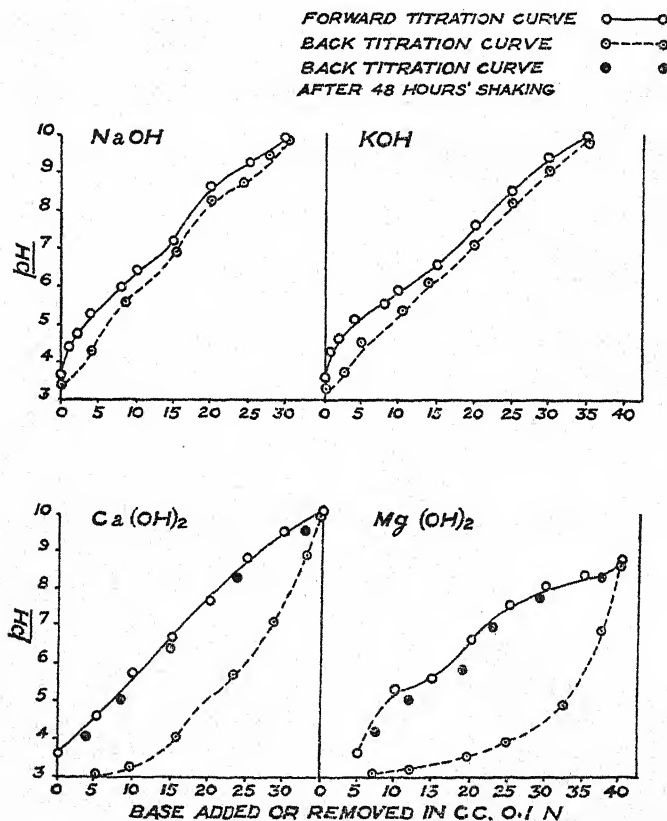


FIG. 3. FORWARD AND BACK TITRATION CURVES OF HUMATES

do not exist as individual molecules but as compound particles, the molecular forces of cohesion resulting in a stable structure which is not broken down in ordinary mechanical analysis. When alkali is added to these compound particles, the molecules near the surface are neutralized to a much greater extent than are those toward the inside. The pH registered is, therefore, too high, and it gradually adjusts itself to a lower value on shaking. On the other hand, when alkali is removed from the soil, it comes mostly from the surface molecules. The pH registered is, then, too low, and it gradually

risers as the alkali from the inner molecules slowly diffuses out. This view, if correct, leads to a very important conclusion, namely, that exchangeable ions are diffusible, and the establishment of equilibrium leads to a uniform distribution of the exchangeable ions throughout the soil mass. It follows also that if this equilibrium is disturbed by the removal of ions from one portion, it must lead to the migration of ions. In other words, if plants make use of the exchangeable bases from the part of the soil in immediate contact with the root hairs, more of these bases must travel from other parts to make up the deficiency. Exchangeable bases, therefore, can behave like soluble salts in this respect.

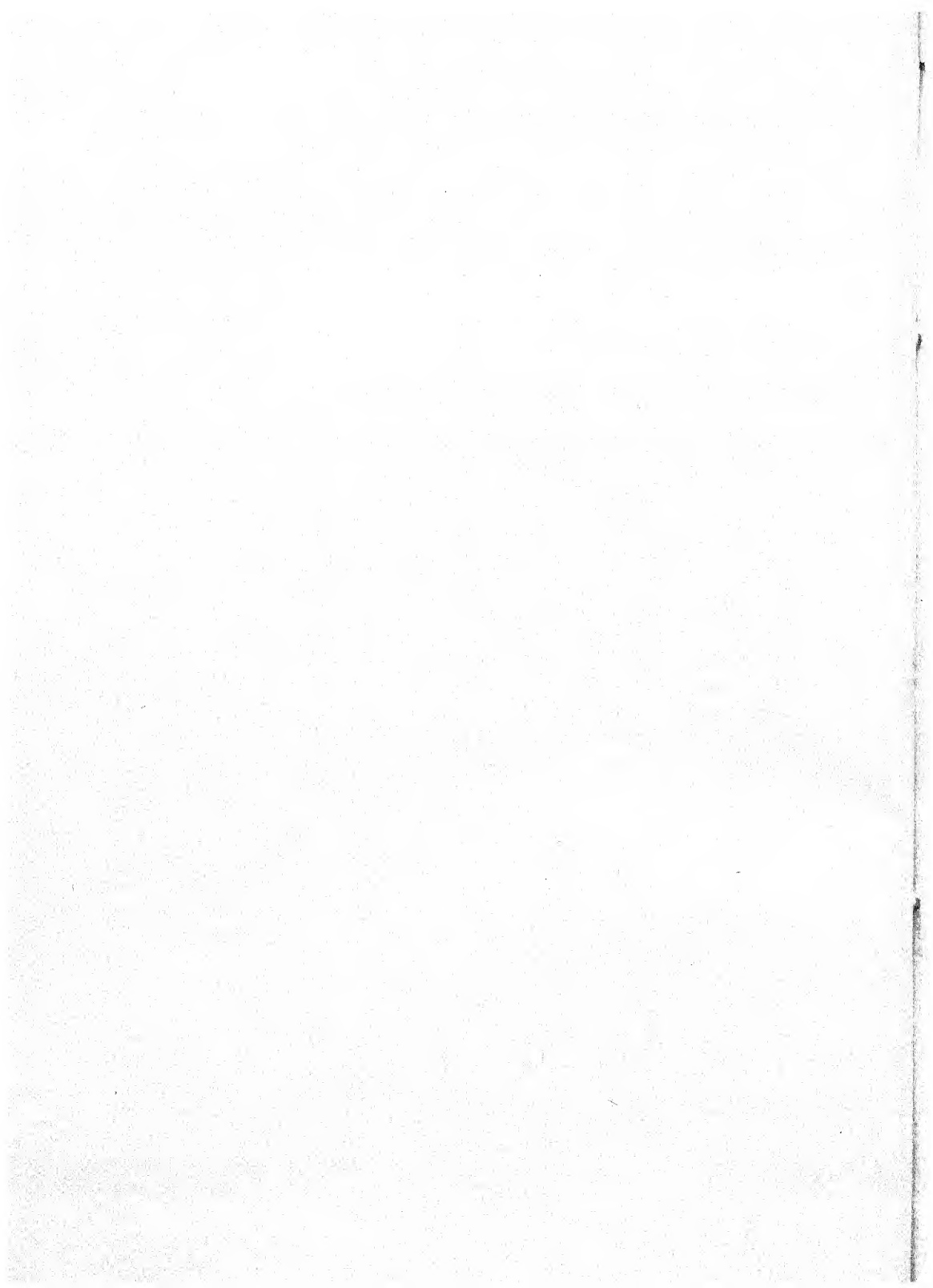
Electrodialysis of humates

Humates of Na, K, Ca, and Mg were prepared by the addition of equivalent amounts of alkalies followed by shaking for 48 hours. In one set of experiments alkali was removed continuously, and the pH value of the alkali removed was determined at definite intervals. Ca- and Mg-humates, like the soil suspensions, were also shaken for 48 hours after every removal of alkali. In every case, 0.5 gm. of humus was taken for electrodialysis. The forward and the back titration curves are given in figure 3. The general similarity between the soil and the humus curves is at once apparent. Likewise the back titration curves are identical to the forward curves, provided sufficient time is allowed for attainment of equilibrium after the removal of any portion of the alkali. It is to be noted that Na- and K-humates show only a very slight shift of the back titration curves even without shaking. This is in conformity with the view that humates of alkali metals are soluble in water.

It is convenient at this juncture to point out that a part of the alkali, especially the Ca and Mg, displaced by electrodialysis, sticks to the cathode and must be removed by acid treatment every time the alkali is determined. Simple titration of the electrodialyzate may lead to very erroneous results. For instance, as little as 10 per cent of the Mg may come down in the electrodialyzate, the rest sticking to the cathode. The exact mechanism of this deposition of bases on the electrode is under investigation. In the meantime, the importance of taking account of this portion of the electrodialyzed bases must not be overlooked.

SUMMARY

Back titration curves of single-base soils and humates were determined by electrodialysis. These curves are identical to forward curves, provided the suspension is shaken for 48 hours after every incremental removal of alkali.



MEETINGS OF THE THIRD COMMISSION OF THE INTERNATIONAL SOCIETY OF SOIL SCIENCE

The Third Commission of the International Society of Soil Science, concerned with the subject of soil microbiology, will hold meetings in New Brunswick, N. J., from August 30 through September 1 on the campus of the New Jersey Agricultural Experiment Station and Rutgers University. Papers will be presented on three subjects: Legumes and Legume Bacteria; Microbiology of Soil Organic Matter; and Azotobacter and Its Significance in Soil Processes.

The program on August 30 will deal with the subject Legumes and Legume Bacteria, on which reports will be given by the following members: W. A. Albrecht, University of Missouri; F. E. Allison, U. S. Department of Agriculture, Washington, D. C.; A. Demolon, Centre National de Recherches Agronomiques, Versailles, France; J. Dufrenoy, Université de Bordeaux, France; H. Katznelson, New Jersey Agricultural Experiment Station; L. T. Leonard, U. S. Department of Agriculture, Washington, D. C.; K. V. Thimann, Harvard University; H. G. Thornton (President of the Commission), Rothamsted Experimental Station, England; W. W. Umbreit and P. W. Wilson, University of Wisconsin; A. I. Virtanen, Biochemical Institute, Finland; A. L. Whiting, The Urbana Laboratories, Urbana, Ill.

The subject of Microbiology of Soil Organic Matter will be discussed by the following members on the morning of August 31: Chr. Barthel and N. Bengtsson, Lantbrukshögskolan, Sweden; F. E. Clark and Charles Thom, U. S. Department of Agriculture, Washington, D. C.; D. Fehér, Institute of Forestry, Hungary; H. Murata, Kogoshima Imperial College of Agriculture and Forestry, Japan; A. G. Norman, Iowa State College; C. E. Skinner, University of Minnesota; S. C. Vandecaveye, Washington State College; S. A. Waksman, New Jersey Agricultural Experimental Station; J. Marszewska-Ziemiecka, The National Institute for Agricultural Research, Poland.

During the afternoon of August 31, papers will be presented on the subject Azotobacter and Its Significance in Soil Processes by the following members: G. Guittonneau, Institut National Agronomique, France; C. K. Horner and Dean Burk, U. S. Department of Agriculture, Washington, D. C.; H. W. Reuszer, Colorado Agricultural Experimental Station; R. L. Starkey, New Jersey Agricultural Experiment Station; M. Winnik and M. Goldberg, Mikveh-Israel Experimental Station, Palestine. A conference will be held on legume inoculants under the direction of A. W. Hofer, of the New York (Geneva) Agricultural Experimental Station.

Following the meetings, on September 1, an excursion will be made to some of the agricultural regions of New Jersey.

The meetings will be held in close cooperation with the Third International Congress for Microbiology, which is to be officially opened on September 2. Anyone wishing information concerning the program and arrangements during the period of the meeting should communicate with R. L. Starkey, Agricultural Experiment Station, New Brunswick, New Jersey.

THE TRANSFORMATION OF PHOSPHORUS DURING THE DECOMPOSITION OF PLANT MATERIALS¹

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Organic materials that are likely to reach the soil generally contain considerable phosphorus, ranging from 0.1 to 0.5 per cent (1, 2, 4, 5, 7, 14, 16, 17, 18, 19, 21, 23). Much of the phosphorus in the materials is in organic combinations which are not readily available to plants; the release of this great quantity of phosphorus in the form of readily available phosphate depends upon the decomposition of the organic compounds by microorganisms. From the point of view of phosphorus conservation, farm manures, green manures, and composts of various organic residues should not be considered merely as a source of nitrogen. The idea that phosphorus is completely mineralized during the decomposition of organic matter and can all be absorbed by the plant is too generally accepted.

Despite the many interesting studies on the biological solution of insoluble mineral phosphates, on the assimilation of phosphorus by soil fungi and bacteria, on the presence and abundance of organic phosphorus compounds in the soil, and on the microbial reduction of phosphate, the biological transformation of phosphorus, particularly that phase concerned with the formation and mineralization of organic phosphorus, during the decomposition of plant residues and green manures and during the composting has been the subject of but little investigation.

Working with different kinds of stable manure as sources of phosphoric acid, Egorov (9) noted a reduction in the amount of inorganic phosphates in the unsterilized fermenting manure. He was led to suggest the biological transformation of inorganic phosphorus to organic phosphorus during the decomposition of the organic matter. Duschekkin (8) pointed out that, in addition to physicochemical absorption of phosphorus in the soil, there is also biological absorption or fixation, which increases with an increase in the amount of organic matter (starch) added and also with the length of time. Doryland (5) pointed out that molds are active in the assimilation of plant-food constituents during the first stage of decomposition of crop residues when there is a high energy nutrient ratio; the molds may later play just as important a part as

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do bacteria in liberating plant-food constituents when the ratio is low. Tott-ingham and Hoffman (22) showed that during a period of fermentation of 4 to 6 months, the water-soluble phosphoric acid in manure and in a manure-floats mixture decreased. The reduction was thought to be due to the formation of nuclein compounds by the bacterial cells. The phosphorus thus made unavailable was eventually released in an available form as a result of the action of bacteria on the dead microbial cells after most of the readily decomposable material had been used up. Hutchinson (13), Heck (11), and Tam and Magstad (20) obtained similar results and held the same point of view. The recent data presented by Lockett (15) show an increase in the amount of inorganic phosphorus during the process of decomposition of rye and oat plants. A reversal was obtained after decomposition of the materials for 80 days.

It seemed desirable, therefore, to determine quantitatively what happens to the phosphorus originally present in, or added to, the organic materials when these undergo microbial decomposition. Such a study might be expected to provide information regarding the biological nature of the transformation of phosphorus during the decomposition of the organic matter and the availability of the phosphorus undergoing transformation. The results reported in this paper deal with the transformation of phosphorus during the decomposition of complex organic materials; the transformation of phosphorus during the decomposition of simple carbohydrates will be reported in another paper. The following points have been particularly emphasized:

1. The formation and mineralization of phosphorus in organic combination.
2. The relation of organic phosphorus to organic nitrogen during the process of decomposition.

EXPERIMENTAL

The materials selected for the study were alfalfa (*Medicago sativa*) and winter wheat (*Triticum vulgare*). Samples were taken at random from the border rows of the fertilizer experimental fields of the station. The plants were removed at the following stages of growth:

- Young plant: alfalfa, 10-12 inches high; wheat, 12-14 inches high.
- Medium plant: alfalfa, just before budding; wheat, just before heading.
- Mature plant: wheat, after threshing.

The fresh materials, after being cleaned of weeds, were chopped into pieces one-half inch long and dried in the air. Known quantities of the air-dry materials were placed in glazed porcelain pots in duplicates or triplicates. Distilled water was added to give a moisture content of 70-80 per cent. For the mature wheat, mineral nutrients were added in addition to various amounts of dipotassium phosphate. A small amount of a 5 per cent suspension of fresh field soil was used to inoculate the materials. All pots were covered with glass plates, and the moisture content was maintained during the incubation. Samples were taken for analysis at different intervals.

For various determinations, appropriate duplicate aliquot portions of well-mixed decomposed material were introduced into weighed containers and reweighed, the difference being the amount of the sample taken for analysis. Total nitrogen, ammonia, nitrate, and total phosphorus were determined on the moist samples. The Kjeldahl method modified to include nitrate was used for total nitrogen, with mercury as a catalyst. Normal potassium chloride solution was used to extract the ammonia which was distilled with magnesium oxide. The nitrate was determined by reduction with Devarda's alloy on the potassium chloride extract after ammonia had been removed. The organic nitrogen was assumed to be the difference between the total nitrogen and the sum of the ammoniacal and nitrate nitrogen. The material for total phosphorus was ashed in the presence of magnesium nitrate and brought into solution according to the methods of A. O. A. C. (3). The volumetric method of A. O. A. C. was selected for the determination of the total and inorganic phosphorus. To extract inorganic phosphorus, Collison's method of HCl-alcohol extraction (5) was followed, 1 per cent HCl-alcohol being used instead of 0.2 per cent for the reasons suggested by Heck and Whiting (12). The moist samples for inorganic phosphorus determination were dried in flasks before extraction. The difference between the total phosphorus and the inorganic phosphorus was taken as the organic phosphorus. The ashing was made at 700°C. in an electric furnace. The results are expressed as averages of duplicates of material dried at 100°C.

Transformation of phosphorus during the decomposition of young and medium plant materials

In order to obtain the amount of material left or undecomposed, each pot was weighed before sampling, and the moisture content was determined. After the samples were taken, the pots were weighed again to give the amount of the material remaining for further decomposition. To calculate the amount of decomposition on the basis of the total material originally introduced into the pot, allowance was made for the material removed previously from each pot.

To correlate the transformation of phosphorus with the decomposition of plant materials a proximate chemical analysis of the materials was made according to the method of Waksman and Stevens (25), as shown in table 1.

No attempt was made to study the microflora developing during the decomposition. Occasional observations showed that certain species of *Rhizopus*, *Penicillium*, *Aspergillus*, and *Trichoderma* were the early invaders. The medium wheat was particularly rich in *Chaetomium*. As the decomposition proceeded further, the decomposed materials gradually became covered with white powdery patches. Microscopic examination revealed the white powder to consist of actinomycetes having long coiled aerial mycelium. These actinomycetes failed to grow on sodium albuminate agar (10, medium 5), but colonies developed with highly branched, straight, aerial mycelium.

Strong evolution of ammonia was detected in the young plant materials at the first period of sampling and in the medium alfalfa at the second sampling. The evolution persisted throughout the entire period of decomposition of these materials. Ammonia was never noted in the decomposition of medium wheat plant. From table 1 it will be noted that the medium wheat had a high content of energy-yielding material and a low nitrogen content. Such an unbalanced ratio leads to the assimilation of all of the available nitrogen.

Young wheat decomposed much more rapidly than any other materials. This is shown not only by the amount of the material decomposed but also by a complete loss of its structural identity. It is interesting to note that the medium plants decomposed more than the young plant materials during the first 14 days, but at 42 days it was the young plants which had undergone more decomposition.

Analyses show that 50-60 per cent of the total phosphorus of the plant materials studied consisted of organic forms of phosphorus. Young alfalfa

TABLE 1
Proximate chemical composition of young and medium alfalfa and wheat plants
(Per cent of dry material)

CONSTITUENT	ALFALFA		WHEAT	
	Young	Medium	Young	Medium
Cold-water-soluble organic matter.....	27.49	24.95	25.34	20.67
Hemicelluloses.....	10.50	10.86	17.56	18.61
Cellulose.....	14.04	18.77	17.27	22.45
Lignin.....	8.62	10.21	6.92	9.62
Total nitrogen.....	3.88	2.39	2.36	1.24
Ash.....	8.50	7.67	7.46	4.49

and wheat plants contained 0.35 per cent and 0.334 per cent total phosphorus, and the medium alfalfa and wheat had 0.227 per cent and 0.260 per cent phosphorus respectively. Because of the high content of nitrogenous materials in the alfalfa, the ratio of organic nitrogen to organic phosphorus is much higher in the legume than in the nonlegume. This ratio becomes lower as the plants get older.

The data presented in tables 2 and 3 reveal an extensive synthesis of organic compounds of phosphorus in the early stage of decomposition of all the plant materials. Except in the young alfalfa plant, the increase of the organic phosphorus content in per cent of total phosphorus was as much as 9 per cent over the content of the original material during the first 14 days of decomposition. There was greater conversion of inorganic phosphorus into organic compounds in the medium plant materials than in the young materials. As decomposition progressed further, more of the organic forms of phosphorus were broken down, resulting in lower contents of organic phosphorus in the residues.

Correspondingly, the percentage of the total phosphorus in the form of inorganic phosphorus increased.

TABLE 2

Transformation of phosphorus during the decomposition of young and medium alfalfa

INCUBATION	TOTAL DECOMPO- SITION	TOTAL P PER CENT OF RESIDUE	INORGANIC P		ORGANIC P		ORGANIC N	ORGANIC N ORGANIC P
			Per cent of residue	Per cent of total P	Per cent of residue	Per cent of total P	Per cent of residue	
<i>days</i>	<i>per cent</i>							
<i>Young plant</i>								
0	0.0	0.357	0.169	47.34	0.188	52.66	3.754	19.97
14	23.17	0.473	0.215	45.45	0.248	54.55	3.880	15.04
28	42.07	0.565	0.243	43.01	0.322	56.99	3.580	11.12
42	54.16	0.729	0.355	48.70	0.374	51.30	4.018	10.74
<i>Medium plant</i>								
0	0.0	0.227	0.093	40.84	0.134	59.16	2.274	16.97
14	33.01	0.355	0.113	31.83	0.242	68.17	2.958	12.22
28	42.04	0.392	0.139	38.01	0.243	61.99	3.290	13.57
42	45.54	0.417	0.195	46.76	0.222	53.24	3.402	15.32

TABLE 3

Transformation of phosphorus during the decomposition of young and medium wheat plants

INCUBATION	TOTAL DECOMPO- SITION	TOTAL P PER CENT OF RESIDUE	INORGANIC P		ORGANIC P		ORGANIC N	ORGANIC N ORGANIC P
			Per cent of residue	Per cent of total P	Per cent of residue	Per cent of total P	Per cent of residue	
<i>days</i>	<i>per cent</i>							
<i>Young plant</i>								
0	0.0	0.334	0.144	43.11	0.190	56.89	2.321	12.22
14	31.30	0.478	0.160	33.47	0.318	66.53	2.970	9.34
28	51.74	0.662	0.251	37.92	0.411	62.08	3.842	9.35
42	58.03	0.760	0.364	47.89	0.396	52.11	4.590	11.59
<i>Medium plant</i>								
0	0.0	0.260	0.127	48.85	0.133	51.15	1.164	8.75
14	37.46	0.443	0.158	35.67	0.285	64.33	1.801	6.32
28	51.68	0.538	0.200	37.18	0.338	62.82	2.552	7.55
42	55.85	0.582	0.230	39.52	0.352	60.48	2.964	8.42

In the course of the decomposition, the ratio of organic nitrogen to organic phosphorus was at first narrowed and then widened again.

It should be mentioned that an increase in the organic or inorganic phosphorus content in per cent of the residue does not necessarily mean an absolute

increase. This may be merely due to the disappearance of respirable materials and to the loss of volatile substances. If either the organic or the inorganic phosphorus is calculated as the percentage of total phosphorus or on the basis of the original material, there may actually be a decrease, as is clearly brought out in tables 2 and 3.

The formation and mineralization of organic phosphorus complexes seem to be affected by the amount of available energy-supplying materials, which are themselves influenced more by the age than by the nature of the plant. In the presence of an abundant supply of these energy-supplying materials, such as hemicelluloses and cellulose, and in the presence of nutrients, there is a vigorous microbial development, resulting in the synthesis of considerable amounts of organic phosphorus compounds at the expense of the available inorganic phosphates originally present in the material. The young wheat and the medium wheat and alfalfa have high contents of hemicelluloses and cellulose; after decomposition had proceeded for some time there was more organic phosphorus in these materials than in the young alfalfa. Furthermore, by reason of the fact that medium wheat was richer in hemicelluloses and cellulose, it maintained its high content of organic phosphorus longer than the young wheat plant during decomposition. When the materials which provide available energy become exhausted or the supply of available energy materials is limited, the microorganisms attack the complex organic compounds which contain phosphorus, including those originally present in the plant material and those present in the dead microbial cells. Part of the liberated phosphorus is re-assimilated, while part of it is transformed into inorganic phosphates, resulting in an increase in the inorganic phosphorus content of the decomposed material. This increase will continue as long as additional energy-yielding material is withheld.

It is also interesting to note that, even during the early stages of decomposition of alfalfa, there is actually a temporary reduction in the amount of available phosphorus, while at the same time considerable amounts of available nitrogen are liberated. This suggests that the inorganic phosphorus in the plant material is in a readily convertible state and also that the organic compounds of phosphorus in the plant material are not readily transformed or that the microorganisms preferentially utilize the inorganic phosphorus. It is apparent that the transformation of phosphorus is affected by the supply of available energy material.

With rapid destruction of the nitrogenous substances and synthesis of organic phosphorus from the inorganic phosphorus, the ratio of organic nitrogen to organic phosphorus becomes narrower. With subsequent mineralization of the organic phosphorus compounds the ratio again becomes wide.

It is to be noted that accompanying the decomposition of such plant materials as young alfalfa and wheat the amount of organic phosphorus increases and the amount of inorganic phosphorus correspondingly decreases. This transformation has been consistently overlooked in the past. Although the

possibility existed that mineralization of phosphorus accompanies the liberation of ammonia during the decomposition of young plant material, this was not found to be the case. The increase in the amount of organic phosphorus at the expense of the inorganic phosphate during decomposition can be ascribed to the synthesis of cell material by the microorganisms effecting the decomposition.

Transformation of phosphorus during the decomposition of a mature wheat straw compost with different phosphorus contents

A series of 12 composts consisting of mature wheat straw were prepared in pots, each of which received 5 per cent calcium carbonate and 2.4 per cent ammonia sulfate and was inoculated with a dilute suspension of fresh field soil. The pots were then divided into four groups of three each and treated as follows:

- I. No K_2HPO_4 added
- II. 0.613 per cent K_2HPO_4 added
- III. 1.225 per cent K_2HPO_4 added
- IV. 2.450 per cent K_2HPO_4 added

The sulfate and phosphate were added in solution. The moisture content of the compost was maintained at 70–80 per cent with distilled water. The pots were covered and incubated at room temperature, or at 20°–23°C. Additional portions of 5 per cent calcium carbonate and 2.4 per cent ammonium sulfate were added to each pot after the first sampling. This was done in order to avoid excessive loss of ammonia which would have occurred if the total amount of the two compounds had been introduced at the beginning. Samples were taken after 14, 39, 67, and 104 days of composting. Representative samples from each treatment were prepared for chemical analyses by combining and mixing 50-gm. portions of each of the moist composts of three replicates.

In order to study the effect of phosphorus application upon the course of microbial decomposition of the straw, the evolution of CO_2 was followed according to the method of Waksman and Starkey (24). Three-gram portions of air-dry ground straw were placed in 300-cc. Florence flasks containing 100 gm. of sand (washed with conc. HCl and chromic acid cleaning solution), and to each flask was added 1 cc. of a 5 per cent suspension of field soil and 141.5 mgm. of ammonium sulfate dissolved in 5 cc. of water. Duplicate flasks received 5 cc. of one of the following phosphorus treatments:

- I. No K_2HPO_4
- II. 10 mgm. K_2HPO_4 (0.333 per cent by weight of straw)
- III. 25 mgm. K_2HPO_4 (0.833 per cent by weight of straw)
- IV. 101 mgm. K_2HPO_4 (3.367 per cent by weight of straw)

Two flasks containing the nutrients but no straw were inoculated and included as blanks. The moisture was brought up to 75 per cent. The flasks were connected to the aeration apparatus and incubated at 28°C. for 59 days; the

CO₂ was determined every day for the first 13 days, after aeration for 1 hour. The course of decomposition as affected by the phosphorus treatments is

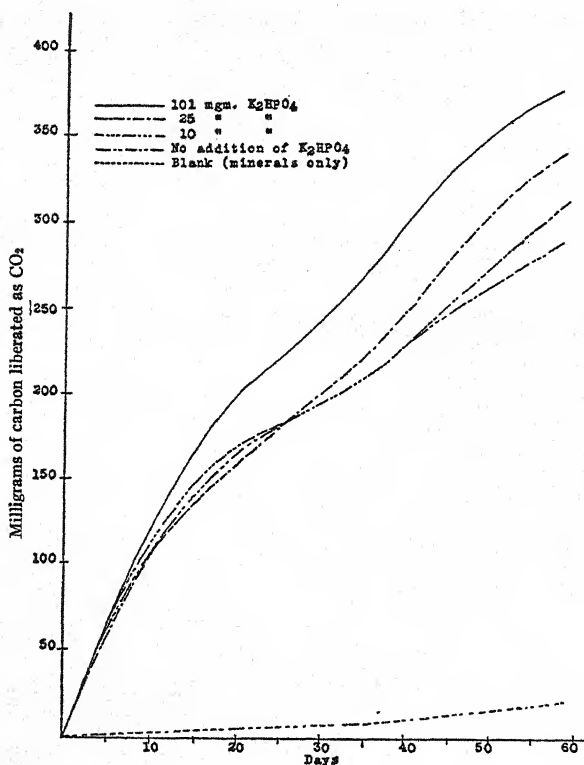


FIG. 1. EFFECT OF PHOSPHORUS UPON THE DECOMPOSITION OF MATURE WHEAT STRAW AS MEASURED BY CO₂ EVOLUTION

TABLE 4

*Effect of phosphorus upon the decomposition of mature wheat straw**

TREATMENT†	TOTAL P ADDED	INOR- GANIC P RE- COVERED	ORGANIC P FOUND	TOTAL N ADDED	NH ₃ - N RECOVERED	ORGANIC N FOUND	ORGANIC N ORGANIC P
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	
No addition of P	2.4	0.0	2.4	42.4	20.5	21.9	9.13
10 mgm. K ₂ HPO ₄	4.2	2.4	1.8	42.4	21.6	20.8	11.56
25 mgm. K ₂ HPO ₄	6.9	3.2	3.7	42.4	18.3	24.1	6.51
101 mgm. K ₂ HPO ₄	20.4	14.6	5.8	42.4	13.8	28.6	4.93

* 59 days of incubation.

† All flasks received 3 gm. ground air-dry straw + 141.6 mgm. (NH₄)₂SO₄.

shown graphically in figure 1, and the results of a chemical analysis of the residual materials are presented in table 4.

After a week of decomposition, the composts in all the flasks were covered with an abundance of heavy white fungus mycelium. *Chaetomium* sp. was found in all flasks during the early stage of decomposition.

After 39 days of decomposition, the pots receiving phosphate turned dark in color. The materials were friable and considerably decreased in volume. The state of decomposition of the materials is clearly indicated by the ash contents at 67 days as presented in table 5 and also by the course of the evolution of CO_2 as graphically shown in figure 1.

TABLE 5

Transformation of phosphorus during the decomposition of a mature wheat straw compost at different phosphorus contents

TREATMENT*	DECOM- POSITION PERIOD	TOTAL P PER CENT OF RESIDUE	INORGANIC P		ORGANIC P		OR- GANIC N	ORGANIC N ORGANIC P	ASH PER CENT OF RESIDUE
			Per cent of residue	Per cent of total P	Per cent of residue	Per cent of total P			
	days								
Original material.....	0	0.082	0.040	48.78	0.042	51.22	0.432	10.29	3.79
No K_2HPO_4	14	0.121	0.054	44.63	0.067	55.37	1.056	15.76	10.79
	39	0.128	0.039	30.47	0.089	69.53	1.450	16.29	15.50
	67	0.151	0.037	24.51	0.114	75.49	1.790	15.70	18.23
	104	0.154	0.048	31.17	0.106	68.83	1.870	17.67	20.96
0.613 per cent K_2HPO_4	14	0.242	0.126	52.07	0.116	47.93	1.220	10.52	11.10
	39	0.265	0.129	48.68	0.136	51.32	1.520	11.18	16.68
	67	0.310	0.151	48.71	0.159	51.29	1.840	11.57	20.51
	104	0.325	0.181	55.69	0.144	44.31	1.900	13.19	21.80
1.225 per cent K_2HPO_4	14	0.394	0.272	69.04	0.122	30.96	1.097	8.99	11.92
	39	0.417	0.247	59.23	0.170	40.77	1.560	9.18	16.78
	67	0.466	0.311	66.74	0.155	33.26	1.800	11.61	21.01
	104	0.483	0.343	71.02	0.140	28.98	1.780	12.71	22.67
2.450 per cent K_2HPO_4	14	0.689	0.507	73.58	0.182	26.42	1.150	6.32	13.18
	39	0.714	0.476	66.67	0.238	33.33	1.680	7.06	19.45
	67	0.807	0.624	77.32	0.183	22.68	1.820	9.94	23.22
	104	0.864	0.690	79.86	0.174	20.14	1.830	10.52	24.26

* In addition to 10 per cent CaCO_3 , 4.8 per cent $(\text{NH}_4)_2\text{SO}_4$, etc.

From table 5 it will be observed that the addition of inorganic phosphate greatly stimulated the decomposition of the mature wheat straw and also led to an accumulation of organic phosphorus. For example, at 39 days the organic phosphorus content of the original straw was raised from 0.042 per cent to 0.089 per cent in the residue receiving no phosphate, to 0.136 per cent in the residue receiving 0.613 per cent phosphate, to 0.170 per cent in the residue receiving 1.225 per cent phosphate, and to 0.238 per cent in the residue receiving 2.45 per cent phosphate.

The synthesis of organic phosphorus is further indicated by the narrowing of the ratios of organic nitrogen to organic phosphorus, namely, from 10.29 in the original material to 6.32 in the material receiving 2.45 per cent phosphate. This ratio became wider with each material as decomposition progressed.

The content of organic phosphorus calculated in per cent of total phosphorus was highest in the compost receiving no addition of phosphate, even after 104 days, indicating in this case that the active microorganisms converted the inorganic phosphorus originally present in the plant material into organic phosphorus and that the organic compounds of phosphorus were inadequate for the requirements of the microorganisms. This emphasizes further that when energy-supplying material is present in abundance, phosphate is assimilated and transformed into organic compounds which accumulate as long as the energy material and the inorganic phosphate do not become exhausted.

It is noted that a small addition of phosphate has little effect on the rate of decomposition, whereas a large dose greatly affects the rate of decomposition; the effect becomes more apparent after long periods of incubation. This effect is further illustrated by the results of chemical analyses presented in table 4, which show that considerable amounts of both organic phosphorus and organic nitrogen were synthesized.

After 104 days the reaction of the residues remaining in all of the pots was close to pH 6.4.

Decomposition of various organic constituents of mature wheat straw at different phosphorus contents

One-hundred-gram portions, calculated on the oven-dry basis, of finely cut mature wheat straw were introduced into 2-liter weighed flasks. To each flask were added 5 cc. of a dilute suspension of fresh soil and 4.72 per cent ammonium sulfate. Duplicate flasks were given one of the following treatments:

- I. No K_2HPO_4
- II. 0.337 per cent K_2HPO_4
- III. 1.236 per cent K_2HPO_4
- IV. 1.236 per cent K_2HPO_4 + 9 per cent $CaCO_3$
- V. 3.372 per cent K_2HPO_4
- VI. 5.131 per cent K_2HPO_4

In addition to these treatments two flasks containing straw alone were inoculated and included in the study. Water was added to the composts to give a total amount equivalent to 300 per cent of the oven-dry weight of the straw. All materials were incubated at 28°C. Samples were taken for study after 60 and 116 days.

The flasks were weighed before and after sampling to ascertain the material left after decomposition and also the material remaining for further decomposition. After each material was thoroughly mixed, aliquot portions were removed for various determinations. Moist samples equivalent to 5 gm. of dry

material were taken for the proximate analysis. The results, calculated on the basis of percentage of the original material, are recorded in tables 6 and 7.

Certain species of *Rhizopus*, *Aspergillus*, *Trichoderma*, *Penicillium*, and *Chaetomium* were found in abundance in all of the composts, the last two species being most numerous. Development of fungi was not nearly so extensive in the flasks containing the straw alone as in the treated flasks.

TABLE 6

Proximate chemical composition of a mature wheat straw compost at different phosphorus contents
(On the basis of original straw)

TREATMENT*	DECOMPOSITION PERIOD	TOTAL DECOMPOSITION	COLD-WATER-SOLUBLE ORGANIC MATTER	HEMI-CELLULOSES	CELLULOSE	LIGNIN
	days	per cent	per cent	per cent	per cent	per cent
Original straw	0	0	5.53	26.80	35.49	16.84
Straw only	60	23.74	3.48	18.13	23.37	15.57
	116	26.52	3.98	16.19	19.67	13.71
Minerals, no P	60	25.98	4.87	16.48	18.56	17.11
	116	30.38	4.41	13.51	15.51	17.81
0.337 per cent K_2HPO_4	60	25.02	4.95	17.49	18.22	17.72
	116	30.89	4.66	13.52	13.62	17.35
1.236 per cent K_2HPO_4	60	25.55	4.55	17.70	16.75	16.11
	116	37.88	4.25	12.10	12.30	17.31
1.236 per cent K_2HPO_4 + 9 per cent $CaCO_3$	60	35.89	2.17	9.41	8.76	16.53
	116	39.50	1.87	7.50	6.16	14.79
3.372 per cent K_2HPO_4	60	32.45	3.79	13.26	14.06	16.23
	116	38.12	3.59	9.90	9.63	17.14
5.131 per cent K_2HPO_4	60	34.40	3.58	11.77	12.57	15.97
	116	43.45	3.38	8.41	7.27	15.10

* In addition to 1 per cent N as $(NH_4)_2SO_4$.

The reaction (pH) of the residues after 116 days was as follows (determined by use of glass electrode): I. 4.05, II. 4.15, III. 4.40, IV. 6.10, V. 4.35, VI. 5.05.

Some interesting facts are brought out by the results in table 6. In general, the addition of phosphate markedly increased the decomposition of various organic constituents of the straw. Whereas the amounts of cold-water-soluble organic matter and lignin were only slightly changed, the hemicelluloses and cellulose suffered pronounced losses, and decomposition was greater where large amounts of phosphate were added. The greatest apparent effect of the phosphate was on the cellulose. The cellulose content was reduced from 35

per cent in the original straw to 7.27 per cent in the compost receiving 5.131 per cent phosphate, after 116 days of decomposition. Hemicelluloses were reduced from 26.80 per cent to 8.41 per cent. Materials receiving small amounts of phosphate did not differ much among themselves or from the compost of straw receiving only nitrogen; the decomposition of the untreated straw was considerably slower than that of any of the treated materials. The

TABLE 7

Transformation of phosphorus during the decomposition of a mature wheat straw compost at different phosphorus contents

TREATMENT*	DECOMPOSITION PERIOD	TOTAL RESIDUE	TOTAL P PER CENT OF RESIDUE	INORGANIC P		ORGANIC P			ORGANIC N PER CENT OF RESIDUE	ORGANIC N	ASH PER CENT OF RESIDUE
				Per cent of residue	Per cent of total P	Per cent of residue	Per cent of total P	Per cent of original straw			
	days	per cent									
Original straw	0	100.00	0.082	0.040	48.78	0.042	51.22	0.042	0.432	10.29	3.79
Straw only	60	76.26	0.098	0.047	47.96	0.051	52.04	0.038	0.580	11.37	5.07
	116	73.48	0.119	0.047	39.49	0.072	60.51	0.052	0.770	9.31	6.57
Nutrients, no P	60	74.02	0.110	0.040	36.36	0.070	63.64	0.052	0.880	12.57	6.40
	116	69.62	0.127	0.044	34.64	0.083	65.36	0.057	1.170	14.01	7.63
0.337 per cent K_2HPO_4	60	74.98	0.165	0.092	55.76	0.073	44.24	0.055	0.900	12.33	6.88
	116	69.11	0.212	0.115	54.24	0.097	45.76	0.067	1.260	12.99	8.09
1.236 per cent K_2HPO_4	60	74.45	0.382	0.243	63.52	0.139	36.48	0.104	1.180	8.49	8.18
	116	62.12	0.483	0.359	74.33	0.124	25.67	0.077	1.410	11.37	9.91
1.236 per cent K_2HPO_4 + 9 per cent $CaCO_3$	60	64.11	0.443	0.206	46.50	0.237	53.50	0.152	0.152	8.61	20.68
	116	60.50	0.471	0.267	56.69	0.204	43.31	0.124	2.120	10.39	22.63
3.372 per cent K_2HPO_4	60	67.55	0.963	0.719	74.66	0.244	25.34	0.165	1.590	6.51	11.32
	116	61.88	1.107	0.879	79.40	0.228	20.60	0.141	1.690	7.41	12.22
5.131 per cent K_2HPO_4	60	65.60	1.485	1.038	69.90	0.447	30.10	0.293	1.740	3.89	15.29
	116	56.55	1.639	1.226	74.80	0.413	25.20	0.234	1.860	4.51	16.35

* In addition to 1 per cent N as $(NH_4)_2SO_4$.

addition of calcium carbonate brought about the greatest decomposition of the water-soluble organic matter, hemicelluloses, and cellulose, not excepting the material receiving the greatest amount of phosphate.

The fact that large amounts of inorganic phosphate may be converted into organic phosphorus, during the decomposition of organic matter rich in energy-yielding material, is further emphasized by the results of table 7. After 60 days of decomposition, in the presence of 5.131 per cent dipotassium phosphate, the content of organic phosphorus was seven times the original amount. Anal-

yses of straw receiving no phosphate or only a small amount showed evidence of synthesis of organic phosphorus but no mineralization during the 116 days. There was appreciable mineralization of organic phosphorus at 116 days only in the composts containing large amounts of phosphate. This may be ascribed to the rapid decomposition of these materials. Calcium carbonate exerted a favorable influence on the decomposition of the straw. More inorganic phosphate was converted into organic phosphorus in the limed straw than in the unlimed straw receiving the same amount of phosphorus. The increase of organic phosphorus can be noted indirectly from the ratio of organic nitrogen to organic phosphorus.

The results obtained from the decomposition of medium wheat plants as well as from the last experiments strongly emphasize the fact that, in the presence of large quantities of energy-yielding material, a considerable amount of inorganic phosphorus is transformed into organic phosphorus. Furthermore, evidence of mineralization appears first in those materials from which the readily decomposable substances are most quickly exhausted.

SUMMARY

A study has been made of the transformation of phosphorus during the microbiological decomposition of alfalfa and wheat at three stages of growth; namely, young, medium, and mature.

In the early stages of decomposition of the plant materials a considerable amount of organic phosphorus was synthesized by microorganisms at the expense of the inorganic phosphorus. This is true irrespective of the nature and the stage of growth of the plants. As decomposition progressed further, the organic complexes of phosphorus were gradually mineralized, the rate of which depended upon the stage of growth rather than upon the nature of the plant. For example, at 42 days the contents of organic phosphorus of the young alfalfa and wheat and the medium alfalfa dropped slightly below their original values, whereas that of the medium and mature wheat remained above the original content. The increases and the decreases of the organic phosphorus were accompanied by corresponding decreases and increases of inorganic phosphorus.

The addition of dipotassium phosphate to mature straw compost markedly increased the decomposition of the straw, as shown by the amount of material decomposed and by the rate of CO_2 evolution.

More inorganic phosphorus was transformed to organic forms during the decomposition of old materials than during the decomposition of young materials. As much as seven times the original content of organic phosphorus was found in straw compost receiving 5.131 per cent K_2HPO_4 for 60 days of incubation. In straw receiving no phosphate or only a small amount of phosphate there is no evidence of mineralization of the organic phosphorus during 116 days of decomposition. Appreciable mineralization of organic phosphorus was apparent only in materials treated with large amounts of phosphate.

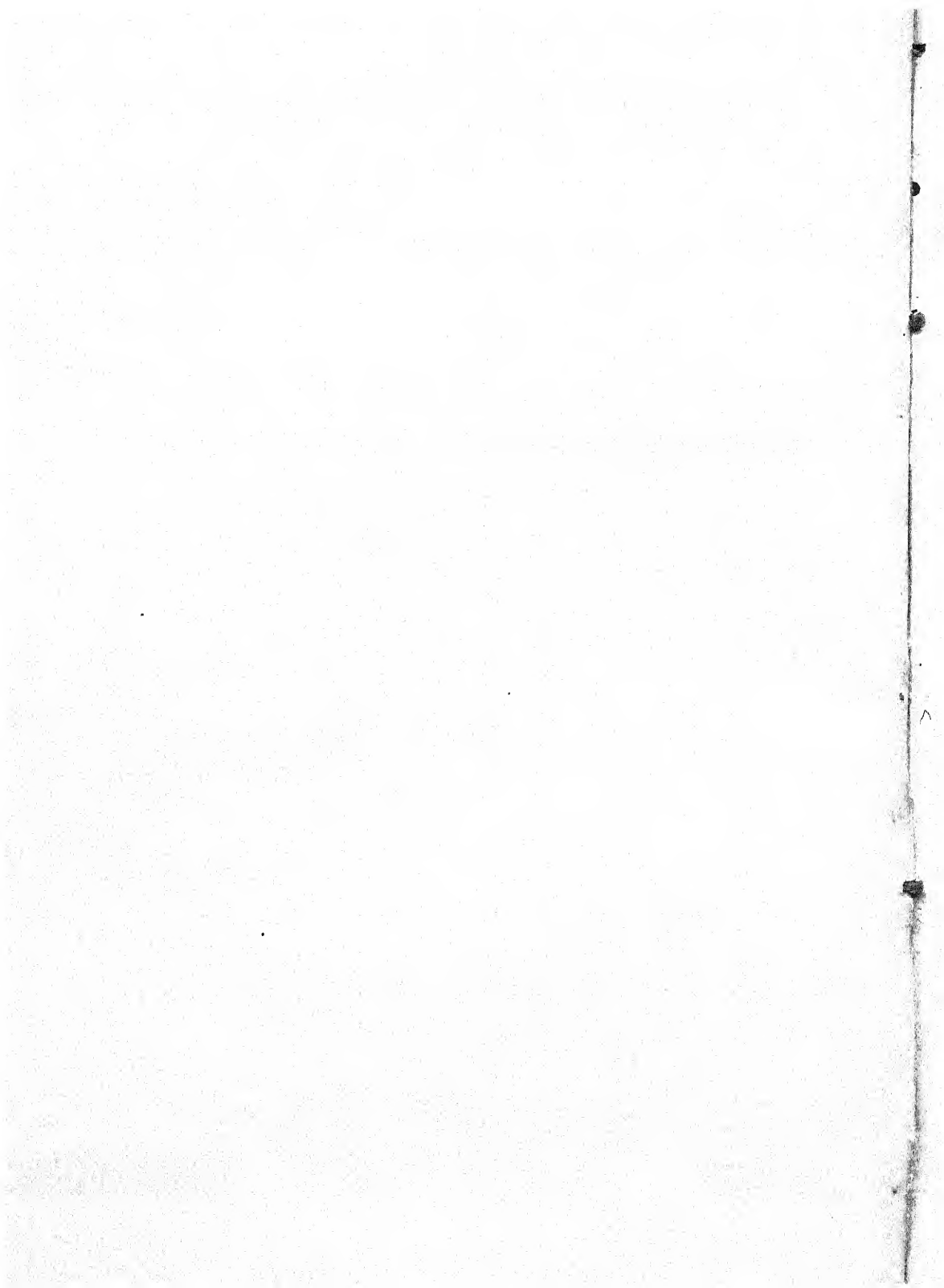
The fractions of the straw most affected by the phosphate applications appear to be the cellulose and hemicelluloses. The decomposition of both fractions was considerable where phosphate was added, whereas the amounts of cold-water-soluble organic matter and lignin were virtually unchanged during the period of decomposition.

The synthesis of organic phosphorus can be further shown by a narrowing of the ratio of organic nitrogen to organic phosphorus. The ratio decreases and increases with the formation and mineralization of organic phosphorus respectively.

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STUDIES IN THE NUTRITION OF VEGETABLES: THE EFFECTS OF VARYING THE POTASH SUPPLY ON SAND CULTURES OF LETTUCE

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Two experiments were made to study the effects of varying the potash supply on sand cultures of lettuce. The plants were grown in fine, white, pure silica sand, described elsewhere (2), seven media being used in each experiment.

The concentrations of important elements present in the media are given in table 1. The salts used in making the media were as follows: sodium nitrate, *AnalaR*, as the source of nitrogen; anhydrous disodium phosphate, *AnalaR*, as the source of phosphorus; potassium sulfate, *AnalaR*, as the source of potassium (and sulfur); a solution of calcium chloride made by neutralization of calcium carbonate, *AnalaR*, with hydrochloric acid, as the source of calcium; magnesium sulfate heptahydrate, *AnalaR*, as the source of magnesium (and sulfur); and ferrous sulfate heptahydrate, *AnalaR*, as the source of iron (and sulfur). The minor elements were found to be unnecessary in these cultures. It will be observed that, for experiment 1, the first six media (A-F) were identical except for a variation in the potassium sulfate content, and that the seventh medium (G) contained potassium and ferrous sulfates only. For experiment 2, the "potash-alone" treatment was omitted and the "no-potash" treatment was expanded to an otherwise complete treatment (GI).

Glazed culture jars, each holding about 46 pounds of sand, were used in the first experiment. In the second experiment, as glazed culture jars were not available, ordinary plant pots holding about 13 pounds of sand were used; the pots were coated outside with three coats of copal varnish and then immersed in boiling "refined" paraffin (m.p. = 110°F.) for 30 minutes.

The lettuce, variety May King, was sown in the sand in the culture jars and pots so that the seed germinated in contact with the medium and there was no transplanting to check growth and develop the coloration of this tinted lettuce (3).

In experiment 1, started on May 25, 1936, there were 12 replications of each of the first five treatments A-E, and the 60 cultures were arranged in an unheated greenhouse as a "layout" of 12 randomized blocks. There were only three cultures each of treatments F (no potash) and G (potash and iron alone),

¹I thank my assistants T. W. McKean and J. F. Leonard for their great help in the routine of these experiments.

and consequently these six cultures were left outside the randomization. During the experiment, 15 liters of medium were supplied to each culture, usually in 500-cc. lots on alternate days. As medium E yielded seedlings of about the same size as those from treatments A, B, C, and D, which all contained more potash, the amount of potash present in medium E was reduced on June 17 to 5.61 p.p.m., on June 26 to 2.81 p.p.m., and on July 1 to 1.12 p.p.m.; the resulting concentrations of sulfur then present in E were 29.23, 28.08, and 27.39 p.p.m.

The second experiment was begun on June 30, 1937. In the randomized arrangement the seven treatments were replicated 16 times, making 112 cultures. During this experiment $8\frac{1}{2}$ liters of medium were applied to each cul-

TABLE 1
Concentration of certain elements in the media

MEDIA	N	P	K	Ca	Mg	Fe	S	Na
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
<i>Experiment 1</i>								
A	16.48	43.70	89.76	36.12	20.20	0.50	63.73	91.88
B	16.48	43.70	67.32	36.12	20.20	0.50	54.53	91.88
C	16.48	43.70	44.88	36.12	20.20	0.50	45.33	91.88
D	16.48	43.70	22.44	36.12	20.20	0.50	36.13	91.88
E	16.48	43.70	11.22	36.12	20.20	0.50	31.53	91.88
F	16.48	43.70	0	36.12	20.20	0.50	26.93	91.88
G	0	0	44.88	0	0	0.50	18.69	0
<i>Experiment 2</i>								
AI	16.48	5.46	44.88	18.06	5.05	0.50	25.35	35.18
BI	16.48	5.46	22.44	18.06	5.05	0.50	16.15	35.18
CI	16.48	5.46	16.83	18.06	5.05	0.50	13.85	35.18
DI	16.48	5.46	11.22	18.06	5.05	0.50	11.55	35.18
EI	16.48	5.46	5.61	18.06	5.05	0.50	9.25	35.18
FI	16.48	5.46	0.56	18.06	5.05	0.50	7.18	35.18
GI	16.48	5.46	0	18.06	5.05	0.50	6.95	35.18

ture, usually in 250-cc. lots three times a week. As the low phosphate content of the media tended to produce purple flushes as the lettuce matured (2, 3), the sodium phosphate content was quadrupled on August 16, so that the media all contained 21.85 p.p.m. of phosphorus. The cultures rapidly became green again (3).

OBSERVATIONS ON THE CULTURES

May 25, 1936: seeds sown for the first experiment; June 3, 1936: germination complete; June 3, 1936: the seedlings were singled; July 10, 1936: harvest.

June 30, 1937: seeds sown for the second experiment; July 6, 1937: germination complete; July 8, 1937: the seedlings were singled; August 31, 1937: harvest.

Summaries of the notes made during the experiments follow:

The seedlings at germination in the first experiment were green; in two days with G (potash alone) the seedlings were darker and tinged with red at the edge. As the experiment progressed, these plants were the darkest of all the cultures, but later became dull bronze. The plants were stunted, with flat, smooth leaves, and had a typical flat, rosette appearance.

During growth a slight deepening in shade developed in passing from A-F, although the green of the F cultures (no potash) was never so dark as that of G. Ultimately the cultures with F turned chlorotic green.

After about 3 weeks the cultures with F (no potash) had a very characteristic appearance. The leaves were smaller than those of normal plants and had wider veins. Likewise, they were not so flat; this was not due to a wavy leaf as a whole, but to the fact that the portions between the veins all tended to be convex on the upper surface, so that a "crinkly" and typically "starved" appearance resulted. These convex portions were darker green than was normal; but later, as previously stated, the plants became rather chlorotic in appearance. Finally the leaf margins also tended to curl upward. As a result of scorch the cultures with F presented a typically tall, narrow appearance.

In the second experiment not much difference in tint was noticed among the cultures. The treatments with least potash gave plants of an abnormally erect habit of growth, as a result of scorch.

Scorch appeared in the first experiment on cultures with E and F after about 4 weeks. Brown dead patches (showing up the network of the leaf structure) and marginal scorch appeared on the outer leaves. These symptoms were followed by limpness and finally by absolute withering of the whole leaf. The scorch due to this deficiency or absence of potash always worked inward from the oldest leaves toward the heart. All the E cultures were severely attacked, but the disappearance of the outer leaves of some of the cultures left lettuce which could be placed in Grade I at harvest. The cultures with F (no potash) were so consistently and badly affected, and the outer leaves withered so rapidly, that all growth seemed to be upward, and a characteristically high, narrow, erect plant finally resulted, as has already been mentioned.

In the second experiment, somewhat similar effects were obtained, but earlier, especially with treatments EI, FI, and GI. Similar marginal scorch extended inward, and patches of scorched tissue broke away and left holes in the leaves. As the older leaves withered and died off, the plants were, at times, not so poor in appearance. The treatment without potash (GI) did not lead to such immature, small, erect plants as those in the first experiment, possibly because, as perceived from the size and weight, the plants receiving treatment GI must have obtained some potash from somewhere. As "spot" tests failed to show the presence of potash in the sand, this potash might have come from the plant pots which, at the end of the experiment, were found to be wetted by water despite the boiling in wax that they had undergone; or

alternatively the sodium present might have replaced potassium to some extent.

Linear measurements of each culture, that is, the greatest spread and the breadth of the culture at right angles to this, were made weekly. At no time was there much difference with treatments A-E in the first experiment. Treatments F and G, however, gave small cultures. At harvest the means of the measurements, in centimeters, were as follows: A, 22.3 x 20.9; B, 22.2 x 21.4; C, 21.4 x 19.8; D, 21.9 x 20.7; E, 22.6 x 21.3; F, 8.3 x 5.7; and G, 3.0 x 2.0. For the first 3 weeks in the second experiment the treatments with least potash gave the smallest cultures. As the experiment progressed, the sizes became more uniform, until at harvest they were, in centimeters, as follows: AI, 26.1 x 24.1; BI, 25.7 x 23.3; CI, 25.7 x 23.7; DI, 25.0 x 22.8; EI, 25.4 x 23.3; FI, 25.0 x 22.5; and GI, 25.1 x 22.7. The results with GI demonstrated that these cultures were obtaining potash, possibly from the pots, as previously explained. In general, the results confirmed those for the first experiment in the important point that potash over a wide range had apparently little effect on size.

The numbers of lettuce plants which were fully hearted and those which were hearting up (the latter values are in brackets) with the various treatments in the first experiment at harvest follow: A, 9 [3]; B, 6 [6]; C, 7 [5]; D, 7 [5]; E, 8 [4]; F, 0 [0]; G, 0 [0]. Thus, increasing the dose of potash beyond that in E (which showed potash-deficiency symptoms as regards scorch, if not as regards size and weight) did not cause earlier maturity. Corresponding figures for the second experiment at harvest were as follows: AI, 4 [8]; BI, 5 [10]; CI, 4 [10]; DI, 4 [12]; EI, 3 [13]; FI, 0 [16]; and GI, 1 [13]; in addition, 4 of AI and 1 each of BI and CI had flower stems forming, which stopped hearting. The conclusion as regards maturity, drawn from the first experiment, was therefore confirmed.

With A, B, C, D, and E, in the first experiment, the roots were normal, well-developed, and bushy taproots; F gave a small, undeveloped root lacking in fiber; and G gave the smallest roots, with long, coarse, hairlike side-shoots. Similar results were obtained in the second experiment, except that FI and GI were about half the size of the roots with treatments AI-EI.

The numbers of lettuce heads judged to be of first grade at harvest in the first experiment were: A, 9; B, 6; C, 7; D, 7; E, 3; F, 0; G, 0. With A, B, C, and D, the remaining heads at harvest were spoilt by the appearance of flower stems or by immaturity; with E, scorch also was responsible to a great extent. Corresponding results were obtained for the second experiment.

YIELD WITH DIFFERENT TREATMENTS

The data for each culture were too bulky to be reproduced but are available for examination in this laboratory. The analyses of variance (1, p. 15 *et seq.*) were worked out for the fresh and dry weights of the tops (cut off at the junction of top with stalk), roots, and total plants, the top/root ratios for fresh and dry weights, and the percentages of moisture in the tops, roots, and total

plants. The corresponding summaries of results for the two experiments are given in tables 2 and 3, together with the standard errors of the treatment means (1, p. 15 *et seq.*). Arithmetical, not weighted, means have been used when dealing with ratios and percentages (3).

In the first experiment the results for the fresh weights of the tops and total plants were not significant. The weights for the roots, however, were highly significant, although even here the results with media A, B, and C, were significantly equal, and the potassium had to be reduced to 22.44 p.p.m. before an increased root system resulted. It was evident that the fresh weights of the plants were unaffected over a wide range of potassium concentrations, the main response being with the roots, where more potassium than the optimum, 22.44 p.p.m., decreased growth. That some potassium was necessary for good

TABLE 2
Summaries of results of experiment 1

DESCRIPTION OF DATA	TREATMENT MEAN FOR					MEAN OF ALL RE- SULTS	S.E.	F	G
	A	B	C	D	E				
Tops, FW., <i>NS</i>	32.37	34.41	25.93	32.31	29.84	30.97	2.073	4.964	0.112
Roots, FW., <i>SS</i>	8.466	10.03	10.26	12.45	11.09	10.46	0.7018	0.257	0.075
Total plants, FW., <i>NS</i> ...	40.84	44.44	36.19	44.76	40.92	41.43	2.466	5.221	0.186
Tops, DW., <i>NS</i>	2.568	2.772	2.325	2.900	2.713	2.656	0.1326	0.375	0.026
Roots, DW., <i>NS</i>	1.289	1.276	1.323	1.596	1.409	1.379	0.1042	0.024	0.021
Total plants, DW., <i>NS</i> ...	3.857	4.048	3.648	4.497	4.123	4.034	0.2244	0.399	0.047
Top/root, FW., <i>SSS</i>	3.864	3.415	2.654	2.635	2.698	3.053	0.1998	19.08	1.484
Top/root, DW., <i>NS</i>	2.014	2.180	1.784	1.941	1.928	1.970	0.1179	14.80	1.265
Tops; per cent moisture, <i>SSS</i>	92.01	91.85	91.11	90.94	90.86	91.36	0.2102	92.27	76.19
Roots; per cent moisture, <i>SS</i>	84.81	87.27	86.85	87.29	87.24	86.69	0.4932	89.76	72.14
Total plants; per cent moisture, <i>S</i>	90.52	90.82	90.00	89.88	89.88	90.22	0.2471	92.13	74.55

growth of both tops and roots was clearly shown by the results with F (no potash); here absence of potash resulted in small tops, roots, and total plants.

In these experiments the potash applied was available to the cultures. As it is generally understood that comparatively large quantities of potash should be applied to produce good growth of this crop (apart altogether from their use from other considerations, such as resistance to frost and scorch), it can only be assumed that these amounts are necessary because potash is not usually readily available after admixture with the soil.

The corresponding results for the second experiment were highly significant, although here also the results with media AI, BI, and CI, were significantly equal for tops, roots, and total plants, which demonstrated lack of response to potash over a wide range, 44.88-16.83 p.p.m. The decrease only commenced with DI (11.22 p.p.m.); and the roots even with EI (5.61 p.p.m.) were very

good and were statistically equal to those for CI and DI. Although FI and GI were statistically equal, and both were significantly less than for all the other treatments for tops, roots, and total plants, they were still substantially large, and demonstrated that such small amounts of potash as could be derived from the pots and/or sand, even after immersion of the pots in boiling paraffin,

TABLE 3
Summaries of results of experiment 2

DESCRIPTION OF DATA	TREATMENT MEAN FOR							MEAN OF ALL RESULTS	S.E.
	AI	BI	CI	DI	EI	FI	GI		
Tops, FW., SSS.....	45.34	44.98	42.96	39.06	38.58	32.23	33.49	39.52	0.9333
Roots, FW., SSS.....	16.82	16.81	14.75	11.87	12.48	6.449	7.514	12.39	0.8191
Total plants, FW., SSS.....	62.16	61.79	57.71	50.93	51.07	38.67	41.00	51.90	1.618
Tops, DW., SSS.....	2.313	2.294	2.285	2.036	2.028	1.479	1.628	2.009	0.0870
Roots, DW., SSS.....	1.336	1.151	1.151	0.904	0.976	0.488	0.472	0.9254	0.0921
Total plants, DW., SSS.....	3.649	3.445	3.436	2.941	3.004	1.968	2.100	2.934	0.1505
Top/root, FW., SSS....	2.85	2.74	2.98	3.46	3.32	6.61	5.26	3.889	0.4142
Top/root, DW., SSS....	2.03	2.05	2.13	2.44	2.47	4.27	4.26	2.808	0.3162
Tops; per cent moisture, S.....	94.89	94.90	94.69	94.79	94.75	95.39	95.15	94.94	0.1659
Roots; per cent moisture, NS.....	92.20	93.13	92.29	92.47	92.48	92.66	93.79	92.72	0.3655
Total plants; per cent moisture, SSS.....	94.15	94.43	94.07	94.25	94.17	94.96	94.91	94.42	0.1749

Notes: In the first column, "Description of Data," FW and DW denote fresh and dry weights; S, SS, SSS, or NS, indicates that the treatment means in the unpublished tables of analyses of variance, according to Fisher's tables of z , were significant at the 5, 1, and 0.1 per cent levels, or were not significant, respectively.

The treatment means are recorded under the "Treatment Mean for" column subheadings. The mean of all the results for a subtable (which is also the mean of the treatment means) is given in the next column; the standard errors of the treatment means are recorded in the column headed "S.E." The difference between any two of the treatment means in a subtable was taken to be significant when it exceeded three times the S.E.

The "no-potash" (F) and "potash-alone" (G) results for the first experiment are averages of three cultures for each treatment, and are tabulated in the two columns after the column "S.E."; as only the results for treatments A-E were included in the randomized block in this experiment, the mean and S.E. apply only to these five treatments, and not to F and G.

were sufficient for moderately good growth, or that sodium could replace the missing potassium.

It was worthy of note that in both experiments a deficiency of potash demonstrated itself by serious scorch before the deficiency was so great as to lead to a serious diminution in growth.

Somewhat similar results were obtained for the dry weights as for the fresh weights, and there was again a marked lack of response to potash over wide

ranges of concentration. Thus for the tops, roots, and total plants, the results with media AI, BI, and CI were statistically equal in the second experiment, and in the first the corresponding results were not significant (NS). In the second experiment, results with FI and GI were statistically equal, and both were significantly smaller than those with all other treatments in the three comparisons, but even then they were substantially large. The results with F (no potash) for the first experiment, however, demonstrated that absence of potash resulted in stunted growth and correspondingly small dry weights for tops, roots, and total plants.

With the fresh weights, the differences in the top/root ratios for the first experiment were highly significant and demonstrated that, in general, the tops were favored more by increased potash than were the roots, the weights of which were actually increased by reduction in potash to the optimum amount of 22.44 p.p.m.; the corresponding ratios for the dry weights were not significant. In the second experiment the results were highly significant for both the fresh and dry weights and showed that although over a wide range, AI-EI, the ratios were statistically equal (thus going a long way toward bearing out the results of the first experiment), the very small quantities of potash provided by the treatments FI and GI favored the tops rather than the roots.

The results for the moisture contents in the first experiment were highly significant for the tops and roots and significant for the total plants. With the tops, decrease in potash supply below B resulted in a decrease in the moisture content; with the roots the provision of more potash seemed to give no response over a wide range (B-E), but ultimately (treatment A) led to a decrease. The results of the second experiment for tops and total plants (the results with the roots were not significant) also tended to prove the lack of response in this respect over wide ranges of concentration; here a very low concentration of potassium, FI = 0.56 p.p.m., was found to give the highest moisture content, and GI also gave, both for the tops and total plants, results statistically equal to those of FI.

SUMMARY

May King lettuce grown in sand showed very little response to potassium over a wide range of concentration. Small amounts gave moderately good growth, although a complete absence of potash resulted in a small plant. The ready availability of the potassium supplied in culture experiments is possibly responsible for the small amount required as compared with the comparatively large amounts recommended for growth of the plants in soil.

Lack of potash first gave a slightly darker leaf than normal, but later tended to cause chlorosis. Scorch appeared with small amounts of potash, even when these were not small enough to cause an appreciable reduction in size. Absence of potash resulted in such rapid, severe scorch and withering away of the older leaves that ultimately a characteristically small, narrow, relatively tall and erect plant resulted; the portions of the leaves between the abnormally

wide veins were convex on the upper surface and gave the leaves a characteristic wavy appearance; these areas were at first darker green than normal, but later became chlorotic.

Large applications of potash did not induce earlier hearting.

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THE INFLUENCE OF VARYING CATION PROPORTIONS UPON THE GROWTH OF YOUNG COTTON PLANTS

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Investigators seeking an insight into the relationships between soil chemistry and plant response have frequently discounted the value of plant nutrient solution studies. This attitude may be justified when one considers that the disparity between the concentration of chemicals in most nutrient solutions and that of a soil solution is of sufficient magnitude to preclude any comparison. For example, the R_2S_4 solution (4) at one atmosphere concentration which has been widely used in nutrient culture work, has the following concentration of nutrient elements in comparison to the available content of these elements in extracts of productive soils (6) giving high microchemical tests for these same elements:

	R_2S_4 SOLUTION (1.0 ATMOS.)	SOIL EXTRACT HAVING HIGH READINGS
	<i>p.p.m.</i>	<i>p.p.m.</i>
K.....	175	50
Ca.....	360	200
Mg.....	108	12
PO_4 -P.....	140	5
NO_3 -N.....	252	25
SO_4 -S.....	144	25

When one bears in mind that these values for the soils represented *available* nutrients and not just those actually in the soil solution, the differential is even greater. And even though one element in such a nutrient solution was maintained at a level comparable to that existing in soils, it is difficult to conceive that the disparity between the two conditions in the concentrations of other elements present would be without effect upon plant response. It would seem, also, that when a technic of continuous solution renewal is used, the concentration of the nutrient ions should more nearly approach that of the soil solution if any parallelism in the nutritional effects is to be studied.

Furthermore, the degree of active acidity in a nutrient solution must be differentiated in interpreting its effect upon plant response from soil conditions giving a similar acidity reading. Other conditions being equal, plants may be grown in nutrient solutions varying as to pH over a considerable range (pH 4-7) without inducing any significant difference in growth response, and yet

show marked differences in growth in soils adjusted over this same range. Solution culture eliminates the vagaries of the exchange capacity of the colloidal complex of a soil. Thus, a soil with an acidity reading of pH 4.0 indicates that the major portion of such exchangeable bases as K^+ , Na^+ , Ca^{++} , and Mg^{++} have leached out, establishing a new equilibrium in the colloidal complex in which there is an increasing saturation with H^+ , thereby inducing Fe^{+++} and Al^{+++} to enter into the exchange complex in increasing quantities. In fact, these phenomena form the basis for the thiocyanate test for soil acidity, i.e., increasing $[H^+]$ concentration is associated with increasing solubility of tribasic cations. Most nutrient solutions are so constituted that Fe and Al are either absent or present only in relatively minute quantities. Thus, similar hydrogen-ion activities in the two types of substrates may not have parallel effects.

Most nutrient solutions which have been used in physiological balance studies have been calculated on the molecular basis. For the most part, this has been satisfactory, but it has led to difficulties when one wished to introduce a substitution of salts in deficiency studies. Thus, a mol of KNO_3 introduces only one-half as much nitrogen as a mol of $Ca(NO_3)_2$ when the former substitutes the latter in calcium deficiency studies. Furthermore, in many of these nutrient solutions, changes in the cation proportions were accompanied by corresponding changes in anion proportions, making for difficulty in the interpretation of ionic effects. Beckenbach et al. (2) devised a system of nutrient solutions in which the anions and cations were varied independently and thus avoided any such contingency. Unfortunately, however, their nutrient solutions were calculated on the molecular basis rather than the equivalence basis. Since stoichiometrical relationships of ions cannot be ignored in any study involving mineral absorption by plants, it would seem reasonable that the ionic concentration of the external medium should be expressed on the equivalence basis.

In order to take into account the aforementioned considerations, a system of devising nutrient solutions was developed wherein the total ionic concentration was maintained at a comparatively low level, ionic proportions were calculated on the equivalence basis, and the ferric ion was introduced as one of the variable components to aid in simulating soil acidity conditions arising from desaturation of exchangeable bases. It is not suggested that any of the solutions used were "ideal." Although excellent growth of the cotton plant was produced by some of these solutions, it must be conceded that modifications of the solutions might have produced more plant growth. But the value of the study lies not in the searching of a "theoretical ideal," but in the observations of the physiological response of a species to a definite chemical status in the substrate.

TECHNIC

Eighty 2-gallon crocks of washed builders' sand were planted with eight seeds each of a pure line of Rowden 2088 cotton seed on March 22, 1937. On

April 5, all but the three most uniform seedlings in each culture were removed, and the most uniform cultures were selected to receive the 22 different nutritional treatments in triplicate. The application of nutrient solutions was started on April 8, using the constant drip technic (8) with a rate of 2 liters daily.

The nutrient solutions were so devised that the four cations K^+ , Ca^{++} , Mg^{++} , and Fe^{+++} comprised the variables in a system characterized by a pyramidal design which allowed variation in four components while the total

TABLE 1
Proportional parts of component cations in nutrient solutions

SOLUTION NUMBER	PROPORTIONAL PARTS			
	K^+	Ca^{++}	Mg^{++}	Fe^{+++}
1	1	1	1	37
2	1	1	37	1
3	1	37	1	1
4	37	1	1	1
5	1	13	13	13
6	13	1	13	13
7	13	13	1	13
8	13	13	13	1
9	3	3	3	31
10	3	3	31	3
11	3	31	3	3
12	31	3	3	3
13	7	7	7	19
14	7	7	19	7
15	7	19	7	7
16	19	7	7	7
17	3	10	25	2
18	3	25	10	2
19	10	3	25	2
20	10	25	3	2
21	25	10	3	2
22	25	3	10	2

number of proportional parts remained constant. Other ions present were maintained at a constant level in all solutions. Each proportional part was taken as 0.000025 equivalent per liter of nutrient solution. This value for the proportional part was empirically chosen, but it does have the convenience of being equivalent to 1 p.p.m. of potassium or $\frac{1}{2}$ p.p.m. of calcium. It was based on the findings of Bartholomew and Janssen (1) that 1 p.p.m. of potassium in the nutrient solution allows limited growth of the cotton plant but is definitely below adequacy. All nutrient solutions contained 40×0.000025 or 0.001 equivalent per liter of the four cations mentioned. The proportional parts of these four cations in the various nutrient solutions are given in table 1.

These four cations were all added as nitrate salts, supplying, thereby, 0.001 equivalent per liter or 14 p.p.m. of nitrate nitrogen. Phosphorus was added as mono-ammonium phosphate; and sulfur, as ammonium sulfate, each at the rate of 2 p.p.m. Sufficient ammonium nitrate was added that the total nitrogen content of all nutrient solutions was 20 p.p.m., 15.5 parts being supplied as $\text{NO}_3\text{-N}$ and 4.5 parts as $\text{NH}_4\text{-N}$. Boron was added as boric acid, and manganese was added as manganese sulfate, each at the rate of $\frac{1}{4}$ p.p.m. The stock solutions were made up as follows:

SALT	MOLARITY	GRAMS/LITER
KNO_3	0.10	10.1
$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	0.05	10.0
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.05	12.8
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.0333	13.4
$(\text{NH}_4)_2\text{SO}_4$	0.0284	3.75
NH_4NO_3	0.0426	3.41
$\text{NH}_4\text{H}_2\text{PO}_4$	0.0284	3.27
MnSO_4		0.203
H_3BO_3		0.142

(All in same liter
of solution)

The concentrations of the four stock solutions supplying the cations K^+ , Ca^{++} , Mg^{++} , and Fe^{+++} were such that the number of milliliters of these solutions to be added to 4 liters of the respective nutrient solution corresponded exactly with the numbers for the proportional parts of each cation given in table 1. The other stock solution, which contained the P, S, Mn, B, and additional N, was added at the rate of 10 ml. to each 4 liters of nutrient solution in order to provide the desired concentrations.

EXPERIMENTAL OBSERVATIONS

Colorimetric pH measurements were made with Clark and Lubs indicators from time to time on the solutions as made up and as they dripped from the base of the sand cultures. The results presented in table 2 were taken on the afternoon of May 3 and are typical of the results obtained on other dates.

It is to be noted that the solutions, as made up, which were high in iron concentration, were the most acid, some being as low as pH 3.8. Yet, these same high-iron nutrient solutions were the least acid when they dripped from the base of the sand culture. It is known that a predominance of cation absorption over anion absorption (H^+ and OH^- excluded) by a plant induces an increase in acidity of the nutrient medium. The converse situation also holds. Table 2 shows the factors for the amount of increase in hydroxyl-ion activity, as these various nutrient solutions dripped through cultures of growing cotton plants. The relatively large decrease in hydrogen-ion activity, or increase in $[\text{OH}^-]$, in nutrient solutions high in iron is the most striking feature of this table. By way of contrast, the solutions which underwent the smallest de-

crease in hydrogen-ion activity were relatively high in potassium. These data indicate, then, that high iron and low potassium concentrations induce a relatively high proportion of hydrogen-ion absorption for a given amount of anion absorption; whereas, when the supply of K^+ approaches adequacy, the proportion of hydrogen-ion absorption for a given amount of anion absorption is reduced.

TABLE 2
The pH values of nutrient solutions

SOLUTION NUMBER	pH AS APPLIED	pH OF DRIP			FACTOR FOR INCREASE IN HYDROXYL- ION ACTIVITY (AV.)	PROPORTIONAL PARTS OUT OF 40 IN ORIGINAL SOLUTIONS	
		#1	#2	#3		K	Fe
1	3.8	6.8	6.7	6.8	920	1	37
2	4.6	6.7	6.6	6.6	110	1	1
3	4.6	6.6	6.6	6.6	100	1	1
4	4.6	6.4	6.5	6.4	67	37	1
5	4.1	6.8	6.8	6.8	500	1	13
6	4.3	6.6	6.8	6.7	250	13	13
7	4.2	6.7	6.6	6.6	270	13	13
8	4.6	6.4	6.5	6.4	67	13	1
9	3.8	6.8	6.8	6.8	1,000	3	31
10	4.6	6.7	6.6	6.6	110	3	3
11	4.6	6.8	6.5	6.7	110	3	3
12	4.6	6.5	6.4	6.4	67	31	3
13	4.0	6.8	6.6	6.7	490	7	19
14	4.4	6.6	6.5	6.6	140	7	7
15	4.4	6.7	6.5	6.6	150	7	7
16	4.4	6.5	6.6	6.5	130	19	7
17	4.6	6.4	6.5	6.5	73	3	2
18	4.6	6.4	6.4	6.4	63	3	2
19	4.6	6.5	6.4	6.4	67	10	2
20	4.6	6.5	6.4	6.5	73	10	2
21	4.6	6.5	6.5	6.5	79	25	2
22	4.6	6.4	6.5	6.5	73	25	2

It is of interest to note the correlation coefficients between the increases in hydroxyl-ion concentration in table 2 and the respective concentrations of potassium and ferric ions in the nutrient solution:

CHANGE IN $[OH^-]$ CORRELATED WITH	CORRELATION COEFFICIENT
Potassium.....	-.483
Iron.....	.966
K/Fe.....	-.432
Calcium.....	-.278
Magnesium.....	-.279

For 20 degrees of freedom, a correlation coefficient with a value of ± 0.423 is significant and one with a value of ± 0.537 is highly significant (9). It is quite

evident, therefore, that the concentration of the ferric ion was the dominant influence in the substrate upon the change in active acidity arising from differential absorption by the plant. The coefficient involving potassium concentration and the K/Fe ratio barely attained significance. The reason that it was significant at all may be explained by the definite relationship with ferric-ion concentration. When calcium- and magnesium-ion concentrations were correlated with the data for increase in hydroxyl-ion concentration, the coefficients were not significant.

TABLE 3
Green and dry weights of plants

SOLUTION NUMBER	K LEVEL	Fe LEVEL	AVERAGE GREEN WEIGHT PER PLANT	PER CENT DRY WEIGHT	AVERAGE DRY WEIGHT PER PLANT
			<i>gm.</i>		<i>gm.</i>
1	1	37	4.23	22.2	0.94
2	1	1	13.8	17.4	2.39
3	1	1	14.1	18.2	2.57
4	37	1	40.5	17.1	6.90
5	1	13	6.22	21.0	1.31
6	13	13	6.11	21.4	1.31
7	13	13	7.78	21.1	1.64
8	13	1	31.20	17.8	5.55
9	3	31	4.44	21.4	0.95
10	3	3	17.6	17.7	3.11
11	3	3	21.2	18.2	3.86
12	31	3	31.9	17.2	5.90
13	7	19	5.67	21.9	1.24
14	7	7	21.6	18.8	4.04
15	7	7	18.6	19.4	3.59
16	19	7	22.8	18.2	4.14
17	3	2	21.8	17.5	3.81
18	3	2	26.5	16.0	4.23
19	10	2	29.1	17.1	4.99
20	10	2	29.2	17.2	5.04
21	25	2	33.1	16.9	5.61
22	25	2	36.6	16.5	6.04
Difference required for significance			5 per cent level	2.19	0.41
			1 per cent level	2.93	0.55
Standard deviation			±1.39		±0.26

The relationship between the factors for increase in $[\text{OH}^-]$ and the data for average green weight per plant for the respective treatments (table 3) gave a correlation coefficient of -0.717 , which is considerably above the requirement for high significance. Thus, there appears to be a marked inverse relationship between removal of hydrogen ions from the substrate and the growth of the plants. The fact that size of the plants was not taken into account merely makes the observation more conservative, since the smallest plants were produced in substrates in which the greatest change in $[\text{OH}^-]$ was taking place.

Table 3 presents the green and dry weight data of the plants produced under the various nutritional conditions and, also, the difference in green or dry weight per plant required for significance among the plants grown in the different treatments. Plants grown in treatments 1 and 9, high-iron treatments, were the poorest plants. The data indicate the poor growth of these plants, which developed symptoms typical of those which occur under conditions of phosphorus deficiency. The leaves were, relatively, very small; their coloration presented a bronzed appearance; and many of them had necrotic areas on their margins.

There was no significant difference in growth or appearance of the plants in treatments 2 and 3, high-magnesium and high-calcium treatments respectively. Both groups of plants made a moderate amount of growth but showed mottling on the margins of the leaves, characteristic potassium deficiency symptoms.

The plants grown in treatment 4 were the largest in the experiment. In every respect, they appeared to be "normal" and were growing vigorously. It should be reiterated that these plants were receiving only $\frac{1}{2}$ p.p.m. of Ca and $\frac{3}{10}$ p.p.m. of Mg in their nutrient solution, whereas potassium was supplied at 37 p.p.m. This gives an indication of the low concentration of calcium and magnesium necessary in the substrate for cotton plants, provided that this concentration is maintained. Also, the preponderance of potassium supply above the supplies of other cations necessary to induce optimum metabolic activity in the cotton plant is indicated by these data.

Plants in treatments 5, 6, 7, and 8 indicate the marked inhibitory effect of iron on the growth of cotton plants. There is no significant difference between plants grown in solutions 5, 6, and 7 where one-third the total equivalents of variable cations were supplied as Fe^{+++} , regardless of level of supply of other cations. In treatment 8, Fe^{+++} supplies only 1 proportional part, and other cations each supply 13 parts, but growth response more than quadruples that of the previously mentioned three treatments.

Data for the growth of plants receiving solutions 9, 10, 11, and 12 confirm those for the plants receiving the first four solutions. The 3 p.p.m. of K^+ in treatments 10 and 11, however, induced appreciably more growth than did the 1 p.p.m. of K in the corresponding treatments 2 and 3. Also, plants in treatment 12 made appreciably less growth with the 3 parts Fe^{+++} than did those given treatment 4 with 1 part Fe^{+++} .

Treatments 13, 14, 15, and 16 further substantiate the inhibitory effect of Fe^{+++} upon growth of the cotton plant. Thus, with iron supplying 7 out of a total of 40 proportional parts of cations, the proportion of the other cations had little effect on growth. By comparison with plant weights produced in other treatments, e.g. treatment 8, it is apparent that solution 16 supplied sufficient K^+ to induce considerably more growth response than was observed, but, evidently, the seemingly small amount of iron present deterred utilization of the potassium available. In general, the plant responses from these four treatments correspond to those of solutions 5, 6, 7, and 8.

In treatments 17 to 22, inclusive, the iron was maintained at a level of 2

proportional parts in all, while the proportions of other cations were varied. It is apparent that growth response increased with K^+ level, but the more interesting point is the amount of growth made by the plants supplied with only 3 p.p.m. of K. This confirms the work of Bartholomew and Janssen (1) that cotton plants have the capacity to obtain an adequate amount of potassium even when the element is supplied at relatively low concentrations, provided, of course, that the concentration is kept nearly constant.

In order to obtain a better picture of the response of the cotton plant to the cation proportions used in this study, a multiple curvilinear correlation analysis was applied to the data for green weight of plants per culture and cation levels, using the successive approximation technic of Ezekiel (3). It should be pointed out, however, that care must be taken as to the interpretations derived from these regression curves. Certain peculiarities inherent in the experimental data preclude the unmodified use of orthodox deductions. As the total of all independent variables is constant, whenever one of these variables approaches the maximum, all of the others must approach the minimum. Thus, when the supply of one of the cations was 37 proportional parts, the other three were supplied at 1 proportional part each. This contingency is anomalous to the theory of multiple regression, which is based on the assumption that values occurring on any portion of the net regression curve for a given independent variable are associated with values distributed over the entire ranges of the other independent variables. Consequently, a discussion of the curves must take into account the fact that these reflect not only the influence of level of supply of a given cation, but also the effect of cationic balance, i.e., the proportion of the total variable cationic equivalence contributed by a given cation.

The net regression curves obtained are presented in figures 1, 2, 3, and 4. The standard error of estimate of these regression curves is ± 7.34 gm., and the index of multiple correlation has a value of 0.975. Thus, the net regression curves obtained permit 95 per cent (0.975^2) of the variance in growth response to be explained by variance in cation levels.

The indexes of part correlation and part determination were calculated from the net regression curves of figures 1-4. It should be borne in mind that these indexes indicate the relationship between the dependent variable, growth, and a given independent variable after taking into account the corrections for the variance of the regression curves of the other independent variables. These indexes were as follows:

INDEPENDENT VARIABLE	INDEX OF PART CORRELATION	INDEX OF PART DETERMINATION
		<i>per cent</i>
K^+	0.952	90.6
Ca^{++}	0.813	66.1
Mg^{++}	0.747	55.8
Fe^{+++}	0.945	89.3

After the effects of Ca, Mg, and Fe ions as given by the respective regression curves are taken into account, 90.6 per cent of the variance observed in growth response may be ascribed to variance in the level of supply of K^+ . Similar relations hold for the other three varying cations. Potassium and iron

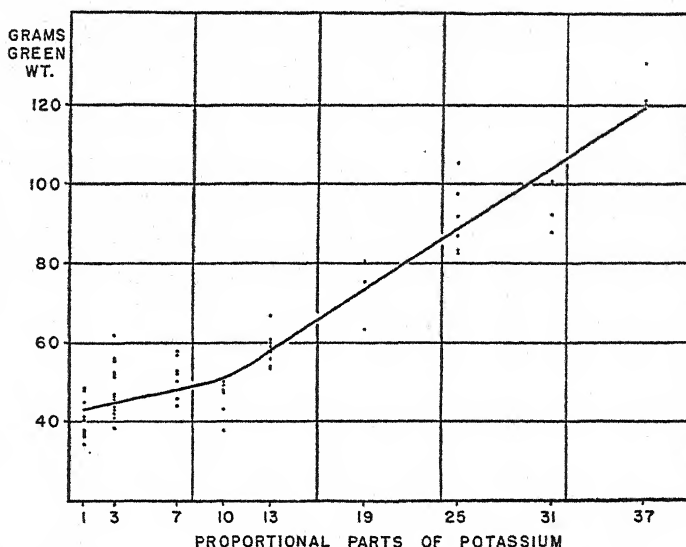


FIG. 1. RELATIONSHIP BETWEEN PROPORTIONAL PARTS OF K^+ SUPPLIED IN NUTRIENT SOLUTION AND THE GROWTH OF COTTON PLANTS, IN GRAMS OF GREEN WEIGHT

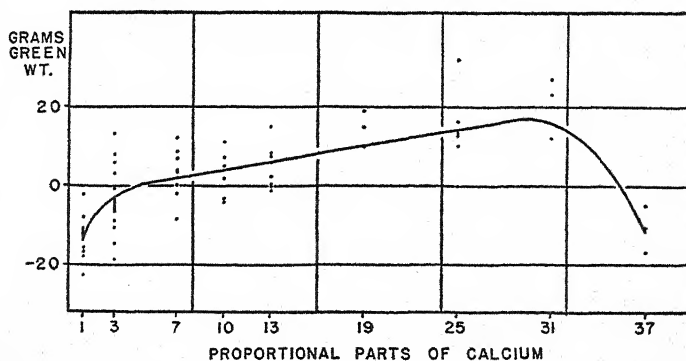


FIG. 2. ALLOWANCE, IN GRAMS GREEN WEIGHT OF COTTON PLANTS, FOR PROPORTIONAL PARTS OF Ca^{++} SUPPLIED IN NUTRIENT SOLUTION

had an appreciably greater effect on growth than did calcium and magnesium, although the influence of the last two ions was pronounced.

The net regression curve in figure 1 indicates that the relationship between growth and potassium supply was positive over the entire range studied, and

evinced the marked growth response to increments in K^+ supply. It is apparent that the optimum level of potassium supply was not attained, and that under the experimental conditions no deleterious effects were associated with the preponderance of cations being supplied as K^+ .

The net regression curve of figure 2 shows that growth response to Ca^{++} was positive over nearly the entire range of Ca^{++} concentrations studied, with a distinct retroflexion in the relationship at the highest level of calcium used. This certainly does not mean that 18.5 p.p.m. of calcium in the nutrient solutions had a detrimental effect on growth as compared to 15.5 p.p.m. It is in accord with the work of Osterhout (7) upon ionic antagonism in relation to permeability and growth; that is, when the preponderance of the cations was supplied as divalent calcium, insufficient monovalent K^+ was present to counteract the injurious effect of the predominance of calcium.

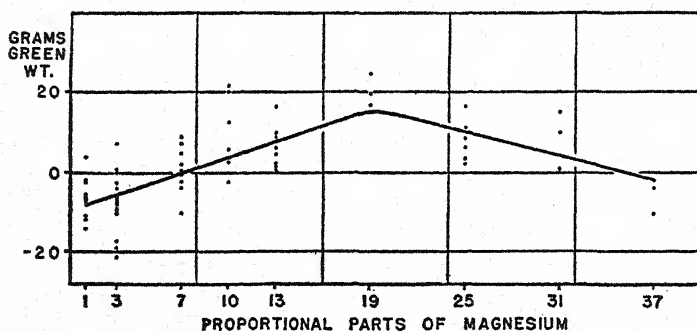


FIG. 3. ALLOWANCE, IN GRAMS GREEN WEIGHT OF COTTON PLANTS, FOR PROPORTIONAL PARTS OF Mg^{++} SUPPLIED IN NUTRIENT SOLUTION

In figure 3, the curve for the magnesium relationship shows the presence of a very definite optimum in the medial portion. Here again, it should not be interpreted that any of the concentrations of magnesium used were sufficient to depress growth *per se*; but when the higher levels of Mg^{++} were used it concomitantly follows that the concentrations of the other three cations approached their lower levels. That is, a preponderance of Mg^{++} even in such dilute concentrations introduces an unfavorable cationic balance.

The net regression curve in figure 4 presents the ferric-ion relationship to growth. The general trend of this curve is negative, with a marked minimum in its medial portion. The effect of cation balance is reflected in this curve. Certainly, increasing the iron content of the nutrient solution from 13 parts to 37 parts is not conducive to a positive growth response. But when only 13 of the proportional parts are supplied as iron, other ions may be present in sufficient amounts to enable appreciable growth were it not for the inhibitive activity of iron. When the preponderance of the cations was supplied as Fe^{+++} , the other cations were not present in sufficient quantity to have permitted appreciable growth in the absence of iron, and, hence, the Fe^{+++} had

less opportunity to effect an inhibitory influence. In other words, the positive portion of the regression curve for Fe^{+++} indicates a decrease in inhibitory effect due to a decrease in growth-inducing potentialities of the supply of other cations, and does not indicate a positive effect on growth by Fe^{+++} .

A discussion of the observed iron relation would have to take into account the results of Mattson's (5) cataphoretic studies on ferric phosphate, which he found to be isoelectric at pH 4.6. The pH range of the nutrient solutions used was such that the higher concentrations of Fe^{+++} would completely precipitate the PO_4 — and cause phosphorus deficiency. As noted earlier, plants receiving high amounts of iron showed symptoms typical of phosphorus deficiency. It is possible that the Hardy-Shulze rule has a bearing upon the relationships found herein. By this rule, the trivalent Fe^{+++} should have a much higher coagulating effect upon the cytoplasmic membranes of the

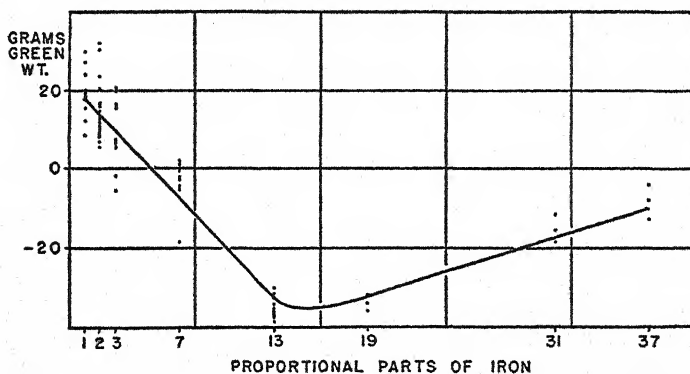


FIG. 4. ALLOWANCE, IN GRAMS GREEN WEIGHT OF COTTON PLANTS, FOR PROPORTIONAL PARTS OF Fe^{+++} SUPPLIED IN NUTRIENT SOLUTION

absorbing roots than the divalent Mg^{++} and Ca^{++} . The last two should have a much greater coagulating effect than monovalent K. A study of table 3 will show that the growth of these cotton plants was inversely related to the charge on the predominating cation. Thus, even though a major portion of this relation can be ascribed to the important nutritional role of K^+ , it does seem that the electrokinetics of membrane phenomena cannot be ignored.

SUMMARY AND CONCLUSIONS

Cotton plants were grown in nutrient solutions varied as to the proportions of potassium, calcium, magnesium, and iron. These nutrient solutions were distinct in that they were relatively very dilute in concentration, only cations entered into the variability, and proportions were calculated on the equivalence basis.

Growth was directly related to level of potassium supply. Increasing the Fe^{+++} supply had a distinctly adverse effect on growth. The influence of

Ca^{++} and Mg^{++} was not so pronounced as that of the other two cations studied. Calcium and magnesium tended to be beneficial unless they supplied a preponderance of the total variable cations.

The pH changes in the substrate were inversely related to the K/Fe ratio; the higher this ratio, the less change in H^+ in the nutrient medium. It was suggested that at the higher levels of Fe^{+++} supply, a larger proportion of cations absorbed, in relation to a given amount of anion absorption, is H^+ .

Of the many theoretical implications of the observed relationships, a few are discussed.

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GROWTH OF CUNNINGHAMELLA BLAKESLEEANA AS INFLUENCED BY FORMS OF NITROGEN AND PHOSPHORUS UNDER VARYING CONDITIONS¹

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The relative growth of the fungus *Cunninghamella* on properly controlled soil cultures has recently been proposed as a measure of the level of available phosphorus in soils (14, 15). Because the method offers considerable promise, a study has been made of the nutrition of this fungus, particularly as regards the suitability of different forms of nitrogen and phosphorus. The results of the investigation are reported in this paper.

Very little specific information on the nutrition of *Cunninghamella* was found in the literature. Previous studies have been restricted largely to morphologic and genetic classification. The forms of nitrogen which various fungi preferably utilize have been widely investigated; for a general review of the literature the reader is referred to the texts of Löhnis (12), Waksman (27), and Lafar (10), and to the papers of Klotz (9), and Janke (8). Whether the ammonium, nitrate, amide, or amino forms of nitrogen are used at all, or with preference, appears to depend upon the fungus, the reaction, the carbon source of the culture medium, and the isoelectric point (17). *Cunninghamella bertholletia* at a slightly acid reaction was able to use the nitrate form rather well (23). In the presence of 1 per cent citric acid and 10 per cent sucrose, *Cunninghamella* sp. apparently was unable to develop with ammonium sulfate as the source of nitrogen (22). *Cunninghamella elegans* and *Cunninghamella echinulata* used the ammonium and nitrate forms equally well at neutral and slightly acid reactions (14).

The usual forms of phosphorus which are supplied to fungi are the salts of orthophosphoric acid, although the meta- and pyro- forms of phosphoric acid and organic forms have been used (3). For a review of the literature on the forms of phosphorus and the extent of their utilization by fungi, the reader is referred to Löhnis (12) and Waksman (27). The assimilation of water-

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insoluble or slightly soluble forms of phosphorus by fungi is closely related to the formation of acid in the metabolic processes of the fungi and partly to the action of enzymes. In the assimilation of phosphorus, reduction may also play a role (18). The acidity of the culture medium influences considerably the assimilation of phosphates by *Aspergillus niger* (25). *Rhizopus* sp. utilized phosphorus from the soil approximately in proportion to the phosphorus soluble in 1 per cent citric acid (21). *Cunninghamella elegans* and *Cunninghamella echinulata* grown in soil cultures near the neutral point developed in proportion to the solubility of the applied phosphates (14).

MATERIALS AND METHODS

The method followed in general in the present work was that of Mehlich, Fred, and Truog (14), in which a solid substratum contained in a small cavity of a special clay dish or slab (15) is used, and the extent of growth of the aerial development of the fungus mycelium (diameter of the colony) is measured directly. *Cunninghamella blakesleeana* (minus strain) was employed (11).

Sand and soil cultures

Optimum conditions for the growth of the fungus in sand cultures were provided by mixing two parts of quartz flour with one part of washed quartz sand. This mixture, from the standpoint of texture, serves as a very satisfactory substratum for growth. Powdered bentonite variously saturated was employed to buffer this sand at different reactions. The use of 6 per cent of natural bentonite containing some free CaCO_3 buffered the system at pH 8.6; a combination of 5 per cent of a 96 per cent K-saturated bentonite and 1 per cent of the natural bentonite buffered it at pH 7.5; and 6 per cent of a 51 per cent K-saturated bentonite buffered it at pH 6.7. By means of H-saturated bentonite, systems at pH 5.3 and pH 2.9 were obtained. The latter was made possible by treating the sand and bentonite mixture with dilute citric acid and washing with distilled water to remove the excess of acid. Systems of intermediate points of reaction were compounded of mixtures of the systems just described. The K- and H-bentonites were prepared by Tyner (26) and Cook (4) respectively. For the determination of pH, the glass electrode and Truog's triplex indicator method were used.

For soil cultures, air-dry surface soil powdered to pass a 20-mesh sieve was used.

Forms of nitrogen used

The inorganic salts of nitrogen, asparagin, aspartic acid, glycine, cystine, and urea used were commercial, chemically pure products; the glutamic acid and arginine were laboratory preparations. The fertilizers were commercial products. The mold tissues were obtained from nutrient liquid cultures. They were washed free of the inorganic salts, and ground to pass a 60-mesh sieve. Alfalfa hay was similarly treated.

Forms of phosphorus used

With the exception of the crude phytin, which was a laboratory preparation, and metaphosphate, which was prepared at Muscle Shoals, all inorganic and organic phosphorus salts used were commercial, chemically pure products. Before being used, the iron and aluminum phosphates were washed to remove the water-soluble portion. The basic iron phosphate—dufrenite—was an impure sample containing 19.2 per cent P_2O_5 ; and before being used it was treated with CO_2 -saturated water to remove any easily soluble phosphorus. The rock phosphate was a 200-mesh commercial product.

Nutrient solution

For convenience, a stock solution of inorganic salts having the following composition was prepared:

K_2SO_4	10.00 gm.
$FeSO_4 \cdot 7H_2O$	0.05 gm.
$MgSO_4 \cdot 7H_2O$	5.00 gm.
$ZnSO_4 \cdot 7H_2O$	0.05 gm.
Distilled water.....	100 cc.

The final nutrient solution was made up fresh each time just before use. For the test with forms of phosphorus, it was prepared as follows:

Sucrose.....	2.5 gm.
Asparagin.....	0.5 gm.
<i>L</i> -Aspartic acid.....	0.1 gm.
Stock solution of inorganic salts.....	0.5 cc.
Distilled water.....	100 cc.

For the test with forms of nitrogen, asparagin and *L*-aspartic acid were omitted, and 0.1 gm. of $CaH_4(PO_4)_2 \cdot H_2O$ was added in all cases.

Addition of different forms of nitrogen and phosphorus

The soluble forms of nitrogen and phosphorus tested were added in the desired concentration to the nutrient solution, of which a definite volume, usually 2 cc., was then added to 10 gm. of sand or soil. The plaque was brought to its optimum moisture content by adding some nutrient solution free of nitrogen or phosphorus. To obtain a satisfactory distribution of the water-insoluble forms of nitrogen and phosphorus with substratum (sand or soil), the required amount of material was first mixed thoroughly in a mortar with a small amount of fine quartz sand, after which this portion was thoroughly mixed with the soil or sand.

INFLUENCE OF FORMS OF NITROGEN AND REACTION ON GROWTH

It was found previously (14) that, within a certain narrow range of reaction, both the ammonium and the nitrate forms of nitrogen are used by *Cunning-*

hamella. In the present study, organic forms of nitrogen were included, and the range of reaction was extended.

After the concentration of soluble nitrogen necessary to obtain maximum growth of the fungus was determined, different forms of nitrogen were added at a rate to provide 5 mgm. of nitrogen per 100 gm. of sand-bentonite mixtures. The results thus obtained are presented graphically in figure 1.

Cunninghamella blakesleeana is apparently able to use the nitrate form equally well throughout a wide range of reaction, whereas the ammonium form

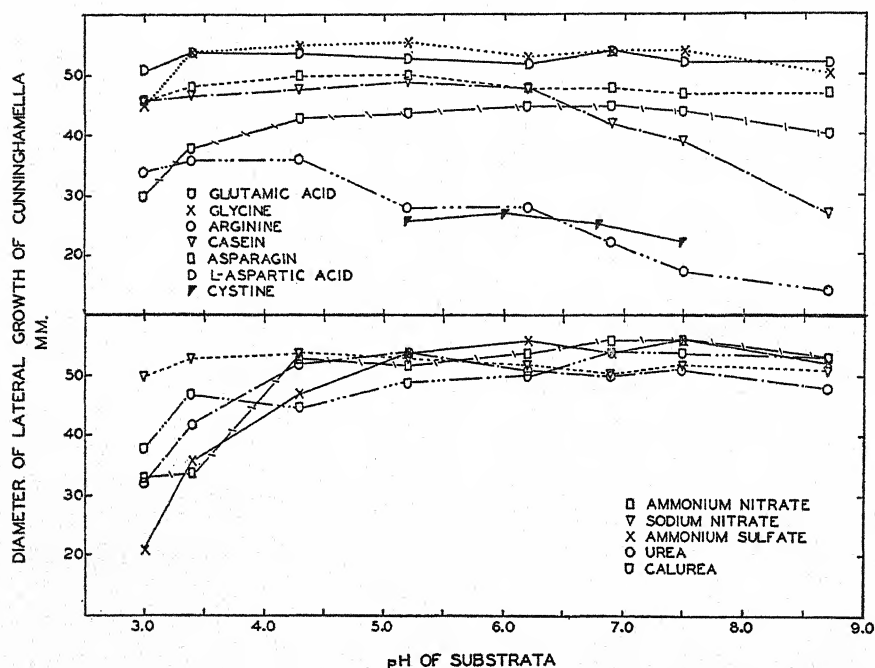


FIG. 1. GROWTH OF *CUNNINGHAMELLA BLAKESLEEANA* IN SAND CULTURES WITH DIFFERENT FORMS OF NITROGEN AND AT DIFFERENT REACTIONS

Rate of application, 5 mgm. N per 100 gm. sand, except cystine, which was applied at the rate of 20 mgm. N per 100 gm. sand.

is used equally well only above pH 5 and to a considerably less extent below pH 4. That ammonium nitrate is not used so well at a reaction more acid than pH 4 is undoubtedly due to the less favorable action of the portion existing as ammonium. It is interesting to note that urea and calurea (containing about one-fifth of its total nitrogen in the nitrate form), both of which yield ammonium on decomposition, influenced growth much as did ammonium sulfate. That reaction plays an important role in the assimilation of different forms of nitrogen by fungi has been clearly demonstrated by Rippel (17), Sakamura (19), and others (12, 27).

Of the monoamino-monocarboxylic acids used, the glycine was utilized equally well at all reactions. Cystine applied at the rate of 20 mgm. N per 100 gm. sand was assimilated only to a slight extent. Of the monoamino-dicarboxylic acids used, aspartic acid permitted maximum growth throughout the range of pH 3.0 to 8.6, whereas the glutamic acid, though not permitting maximum growth, was utilized equally well at all reactions above pH 4. The diamino-monocarboxylic acid, arginine, was utilized to a moderate degree on the acid side and least on the alkaline side. The acid amide, asparagin, was assimilated equally well at all reactions. The casein, containing a variety of amino acids, was utilized best on the acid side.

To determine to what extent *Cunninghamella blakesleeana* can grow in the presence of more complex nitrogenous materials, a number of organic fertilizers, calcium cyanamid, mold, and plant tissues were added to sand-bentonite mixtures. The results obtained are given in table 1. The best growth was ob-

TABLE 1

Relative growth of Cunninghamella on cyanamid and organic forms of nitrogen added on the basis of 20 mgm. nitrogen per 100 gm. sand

REACTION	DIAMETER OF LATERAL GROWTH WITH DIFFERENT NITROGEN SOURCES								
	Calcium Cyanamid	Cotton-seed Meal	Tankage	Dried Blood Meal	Milorganite	Nettolin	Mold Tissue (<i>A. niger</i>)	Mold Tissue (<i>A. sydowii</i>)	Alfalfa Hay
pH	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
5.2	12	45	31	29	40	54	44	53	31
6.0	18	50	26	27	37	54	46	54	34
6.8	17	47	30	31	40	53	40	50	33
7.5	12	48	19	30	40	50	39	50	33

tained with Nettolin (processed peat), which may be due partially to its content of a small amount of nitrate nitrogen. Cottonseed meal, Milorganite (activated sludge product), and mold tissue produced growths approaching that of Nettolin. With calcium cyanamid, no growth was obtained; but with a second sample kept moist for 14 days and then inoculated with spores of *C. blakesleeana*, growth took place as shown. That the fungus can utilize nitrogen from mold tissue and alfalfa hay is also indicated.

The results obtained, in general, would lend support to the idea that *Cunninghamella blakesleeana* might be used for measuring the nitrogen deficiencies of soil. The fungus not only responded to the forms of nitrogen available to plants, namely, nitrate and ammonium, but also to other forms of nitrogen which are considered potential sources for plants.

INFLUENCE OF FORMS OF PHOSPHORUS AND RELATED CONDITIONS ON GROWTH

To study the influence of different forms of phosphorus on the growth of *Cunninghamella blakesleeana*, sand-bentonite mixtures and soils were used as

the substrata. The influence of pH, iron and aluminum oxides, and calcium carbonate on the availability of phosphorus to this fungus was also investigated.

The influence of forms of phosphorus on growth in relation to reaction in sand cultures is shown in figure 2. Of the inorganic phosphates, the mono- and dicalcium phosphates and magnesium phosphate are available throughout

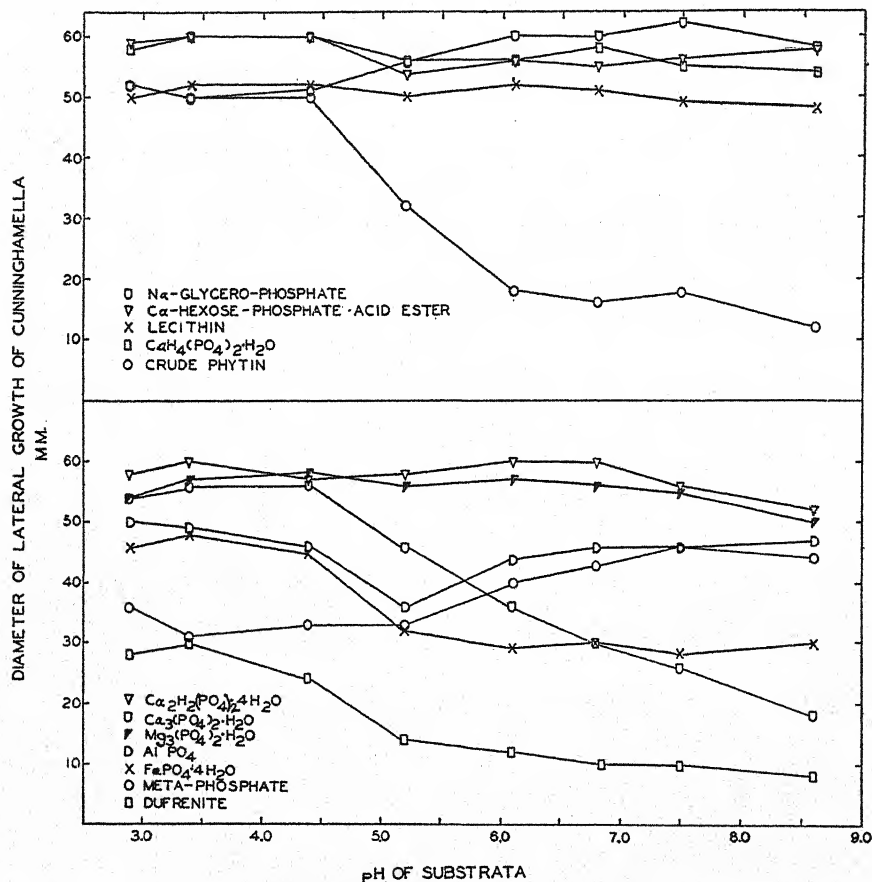


FIG. 2. GROWTH OF *CUNNINGHAMELLA BLAKESLEEANA* IN SAND CULTURES WITH DIFFERENT FORMS OF PHOSPHORUS AND AT DIFFERENT REACTIONS

Rate of application, 5 mgm. P_2O_5 per 100 gm. sand except dufrenite and crude phytin, which were applied at the rate of 20 mgm. P_2O_5 per 100 gm. sand.

a wide range of reaction. Above pH 8 the dicalcium phosphate and the magnesium phosphate produced less growth. The tricalcium phosphate is readily available on the acid side and becomes gradually less available toward the neutral and alkaline side. *Cunninghamella blakesleeana* can use to an appreciable extent the aluminum and iron phosphates and the metaphosphate. Aluminum phosphate and the metaphosphate are absorbed on the alkaline

side better than tricalcium phosphate. Some investigators obtained similar results (1, 13, 24) with plants. That plants can use the metaphosphate has been shown by several investigators (6, 28). With the exception of phytin, which is utilized somewhat better on the acid side, the organic phosphates are readily available throughout the range of reaction studied.

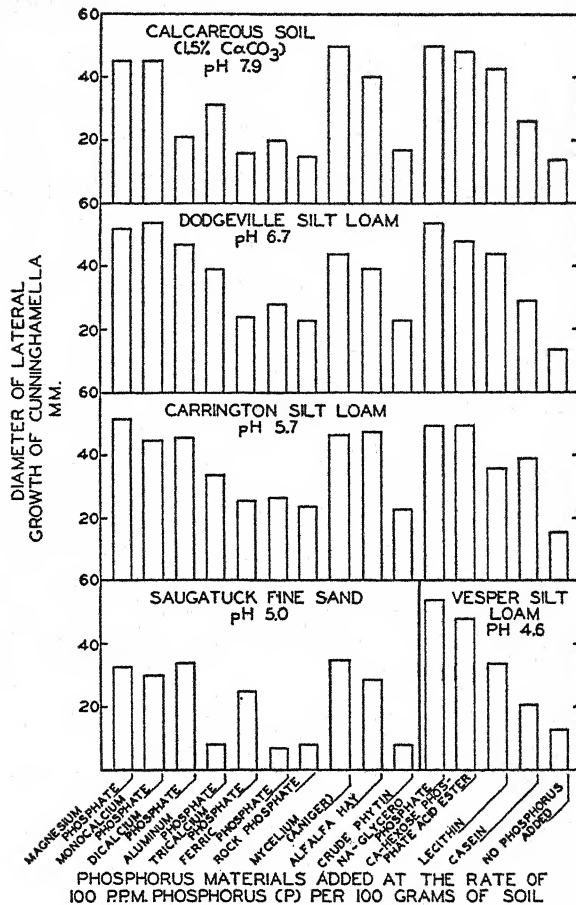


FIG. 3. GROWTH OF CUNNINGHAMELLA BLAKESLEEANA IN SOIL CULTURES WITH DIFFERENT FORMS OF PHOSPHORUS

Figure 3 shows the influence of forms of phosphorus on growth of *Cunninghamella blakesleeana* in soil cultures. The different forms are utilized largely in proportion to their solubility. The presence of free calcium carbonate in a soil renders the tricalcium phosphate appreciably less available and the dicalcium phosphate somewhat less available. Other phosphates, notably the organic forms of phosphorus, are considerably less affected by the calcium carbonate. Saugatuck fine sand has a phosphorus fixing capacity of 80 per

cent, as determined by the method of Heck (7). As a result of this high fixing capacity, the availability of the soluble phosphates applied to this soil for fungus growth was considerably reduced, iron and aluminum phosphates and phytin being used but little.

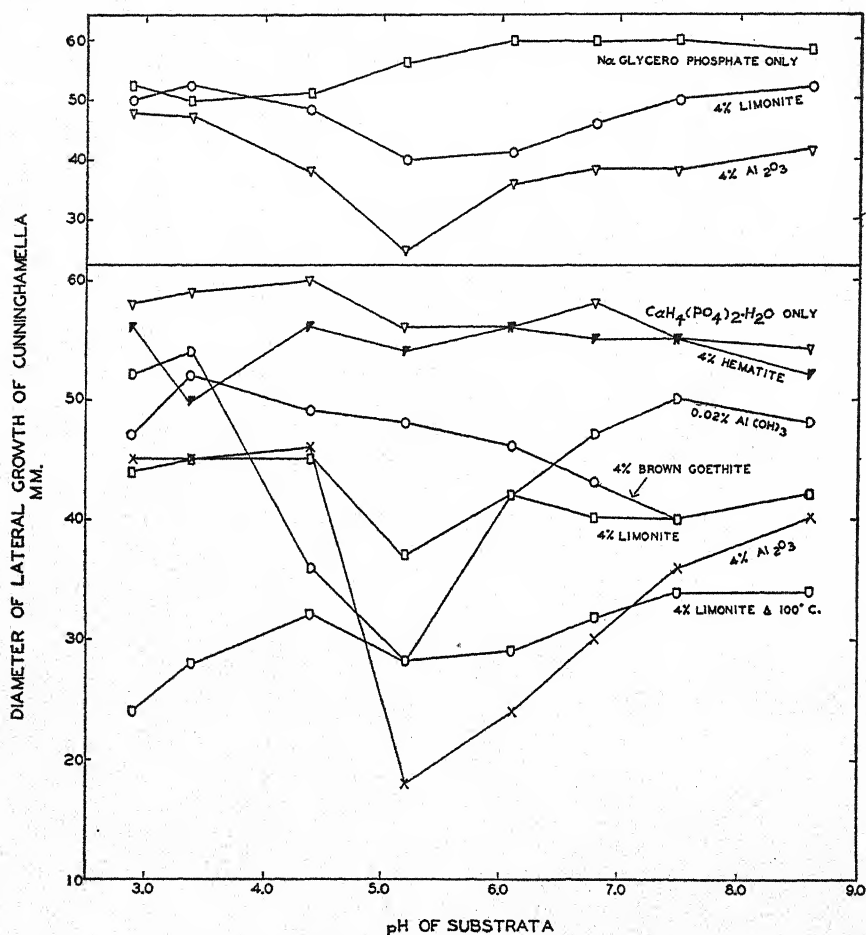


FIG. 4. GROWTH OF *CUNNINGHAMELLA BLAKESLEEANA* IN SAND CULTURES AS INFLUENCED BY IRON AND ALUMINUM OXIDES AT DIFFERENT REACTIONS

Monocalcium phosphate and sodium glycerophosphate were applied alone and with additions indicated at a rate to give 5 mgm. P_2O_5 per 100 gm. sand.

Influence of iron and aluminum oxides on availability of different forms of phosphorus

The extent to which the fungus can use the different forms of phosphorus appears to depend mainly on the solubility of these forms and upon the factors which influence the solubility during the growth of *Cunninghamella blakesleeana*.

leena. To observe how iron and aluminum oxides influence the availability of a soluble phosphate, hematite, goethite, limonite, aluminum oxide, aluminum hydroxide, and diorite were added to sand-bentonite mixtures containing 5 mgm. P_2O_5 per 100 gm. as monocalcium phosphate. The results, given in figure 4, indicate that the growth of *Cunninghamella blakesleeana* was un-

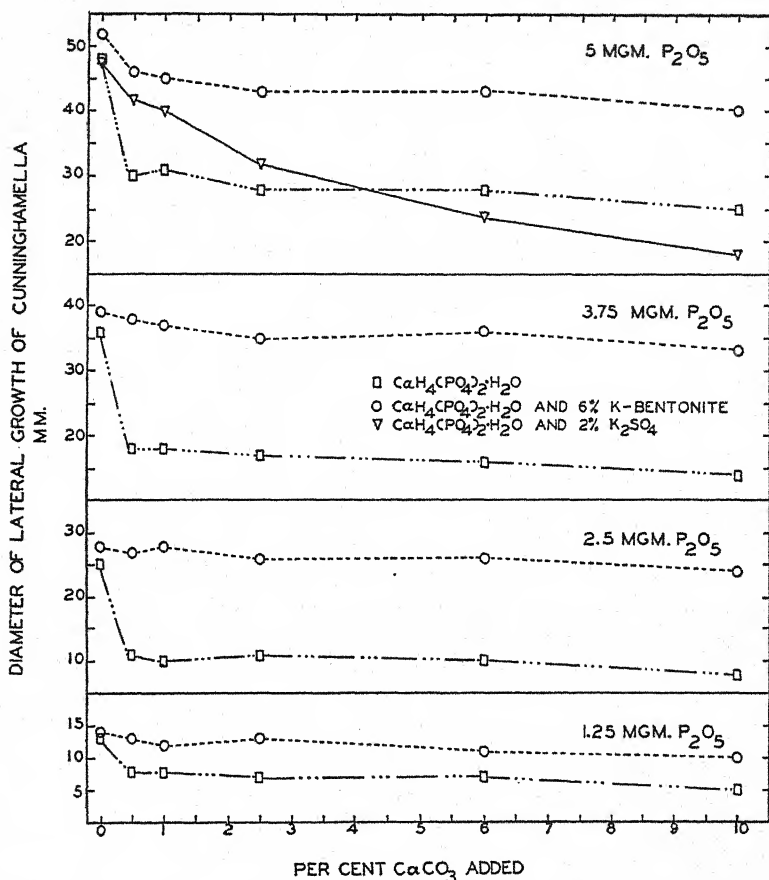


FIG. 5. GROWTH OF CUNNINGHAMELLA BLAKESLEEANA IN SAND CULTURES WITH INCREASING CONCENTRATIONS OF P_2O_5 , AND CALCIUM CARBONATE AND WITH THE ADDITION OF BENTONITE AND POTASSIUM SULFATE

affected by hematite but was slightly reduced by goethite and significantly reduced by limonite, especially when the soluble phosphate was previously dried in contact with the limonite for 12 hours at $100^\circ C$. The aluminum oxide was particularly effective in rendering the phosphorus difficultly available for growth at pH 5.2 and pH 6.1. Colloidal $Al(OH)_3$ (precipitated), added in concentrations of only 0.02 per cent, markedly reduced the availability of

monocalcium phosphate at pH 5.2. In the presence of limonite and aluminum oxide, the availability of sodium-glycerophosphate was also appreciably reduced.

Influence of calcium carbonate on the availability of phosphorus

When to a sand culture containing phosphate but not bentonite, increasing amounts of calcium carbonate were added, growth of *Cunninghamella blakesleeana* was greatly reduced (fig. 5). The presence of 0.5 per cent of calcium carbonate reduced growth nearly 50 per cent. On adding 6 per cent of a 96 per cent K-saturated bentonite, the efficiency of calcium carbonate in reducing the growth of the fungus became appreciably less at all concentrations. The influence of potassium sulfate was similar to that of bentonite when the calcium carbonate concentration was small. At the higher concentrations of calcium carbonate, the soluble salt tended to decrease growth.

DISCUSSION

Under carefully controlled growing conditions of optimum temperature, humidity, and aeration, the growth of *Cunninghamella blakesleeana* can be closely duplicated, and with careful measurements, variations will rarely exceed 10 per cent. This is based on the results of numerous determinations which gave an average deviation of 3 mm. in diameter. In some cases the analysis of variance was used to check the conclusion as drawn from the curves.

The use of different bentonite systems has made it possible to buffer sand cultures sufficiently to prevent any significant changes in reaction due to the addition of different forms of nitrogen and phosphorus. Although the addition of bentonite to systems may have other than buffering influences, serious errors from these influences are not to be expected.

Cunninghamella blakesleeana will grow over a wide range of reaction—pH 2.9 to 8.7 (good growth was obtained on a soil of pH 9.6)—and is not easily influenced directly by acid or alkali, yet it is very sensitive to different forms and concentrations of phosphorus and nitrogen. Ammonium salts and organic compounds like urea, which on decomposition yield ammonium, promote significantly less growth in an acid medium than do nitrate salts. The amino acids promoted the least growth near their isoelectric points, which are for arginine pH 10.8, for glutamic acid pH 3.2, for aspartic acid pH 2.8, and for glycine pH 6.0. This effect is essentially due to the lower solubility of the amino acids near their isoelectric points.

Although *Cunninghamella blakesleeana* grows best on water-soluble forms of organic and inorganic phosphorus, it will grow on some forms of water-insoluble phosphorus, probably because of production of acid in its metabolic processes. The substratum usually becomes slightly more acid below the center of growth than in the surrounding area. Thus, the rate of growth in the presence of soluble phosphorus is rapid from the beginning, but in the presence of water-insoluble forms, it is slow at first, but becomes rapid, usually after 30 hours of incubation.

Factors which influence the solubility of phosphorous will indirectly influence the growth of the fungus. Thus in an acid medium, many water-insoluble phosphates will be readily utilized. The presence of hydrated iron or aluminum oxides greatly reduces the solubility of phosphorus and hence retards growth. This is particularly marked at reactions where insoluble aluminum or iron phosphates are formed. Large amounts of iron or aluminum oxides may influence the availability of phosphorus not only at very acid, but also at moderately basic reactions. Very small amounts of fresh, colloidal $\text{Al}(\text{OH})_3$ decrease the solubility of phosphorus, particularly at pH 5.2 and somewhat less at pH 6.0.

Calcium carbonate reduces the availability of many phosphates to *Cunninghamella blakesleeana*. The effect of calcium carbonate is modified in the presence of a soluble salt or an exchange material containing a monovalent cation. Relatively large amounts of a soluble salt, like K_2SO_4 , at the lower concentrations of calcium carbonate promote growth; at higher concentrations of calcium carbonate this influence was not observed. In the presence of exchange material, the soluble calcium arising from calcium carbonate is removed from the immediate sphere of growth, being replaced by the monovalent cation of the exchange material, and consequently, even at the higher concentrations of calcium carbonate, growth is not significantly reduced.

Although Pierre found that higher plants cannot use organic phosphorus directly (16), other investigators obtained good yields with organic forms of phosphorus that were readily mineralized by microorganisms (2, 20). Phytin can be used by plants largely in proportion to biological activity in which the catalytic action of phytase apparently plays an important part (5). It is significant to note that *Cunninghamella blakesleeana* can use to an appreciable extent only those forms of organic phosphorus which are readily mineralized.

SUMMARY

An investigation of the nutrition of *Cunninghamella blakesleeana* (minus strain), particularly as regards the suitability of different forms of nitrogen and phosphorus under various conditions, was undertaken in both sand and soil cultures. Sand cultures were buffered at different pH values by means of hydrogen- and potassium-saturated bentonites.

The nitrate form of nitrogen promoted the growth of *Cunninghamella blakesleeana* equally well over a pH range of 2.9 to 8.6. The ammonium form, urea, and calurea produced good growth above pH 5 but appreciably less growth with increasing acidity. The monoamino acids, glycine and aspartic acid, gave a maximum growth over a wide range of reaction. Arginine and glutamic acid tended to promote least growth near the pH values of their isoelectric points. Cystine was found to be a poor source of nitrogen for *Cunninghamella blakesleeana*. The fungus was able to make fairly good growth on some complex nitrogenous materials and organic fertilizers which probably contained easily mineralized nitrogen.

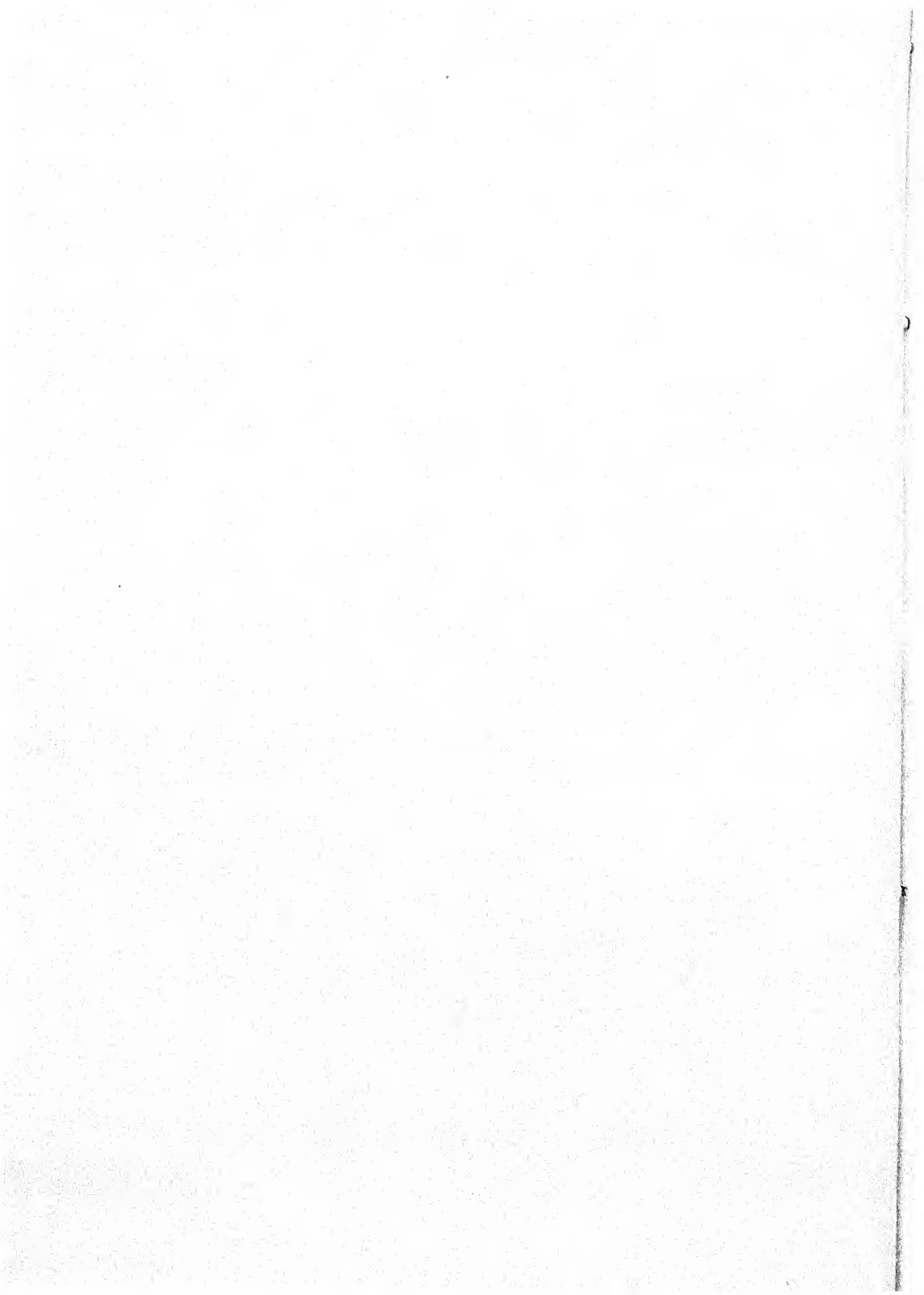
Water-soluble phosphates promoted growth equally well over a wide range of reaction, pH 2.9 to pH 8.6. The utilization of slightly soluble or water-insoluble phosphates varied with reaction, and fairly good growth was obtained on some forms of water-insoluble phosphates. Organic forms of phosphorus were utilized largely in proportion to the ease with which they can be mineralized.

Growth in the presence of water-soluble phosphate was reduced over a wide range of reaction in the presence of 4 per cent limonite, goethite, and aluminum oxide. Freshly precipitated aluminum hydroxide reduced growth markedly at a slightly acid reaction. Calcium carbonate in considerable amounts reduced growth significantly, but at lower concentrations this effect was diminished, especially in the presence of potassium bentonite or a soluble salt like K_2SO_4 .

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AUXIN PRODUCTION BY SOIL MICROORGANISMS

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Nielsen (13) was probably the first to recognize that microorganisms produce plant growth hormones. Prior to his work investigators had isolated 3-indol acetic acid and 3-indol proprionic acid from bacterial fermentations (5, 17, 18), but these compounds were not recognized as auxins. Since the publication of Nielsen's work, several authors have noted the production of auxins by certain yeasts, molds, and bacteria. Table 1 gives a digest of the literature.

TABLE 1
Digest of the literature reporting auxin production by microorganisms

ORGANISM	AUXIN	AUTHOR
Mixed culture.	3-indol acetic acid	Salkowski and Salkowski (18). 1880
Mixed culture.	3-indol proprionic acid	Salkowski (17). 1899
<i>E. coli</i>	3-indol acetic acid.	Hopkins and Cole (7). 1903
<i>Proteus vulgaris</i>	3-indol acetic acid.	Herter and Ten Brock (6). 1909
<i>B. mycoides</i> , several cocci, and members of colon- typhoid dysentery group..	3-indol acetic acid	Frieber (5). 1921
<i>Rhizopus suinus</i> and <i>Absidia</i> <i>ramosa</i>	Not identified	Nielsen (13). 1930
<i>Aspergillus niger</i>	Not identified	Boysen-Jensen (1). 1931
16 species of bacteria.	Not identified	Boysen-Jensen (2). 1931
Brewer's yeast.	Not identified	Nielsen (14). 1931
<i>Boletus edulis</i>	Not identified	Nielsen (15). 1932
Yeast.	3-indol acetic acid	Kögl and Kostermans (12). 1934
<i>Rhizopus suinus</i>	3-indol acetic acid	Thimann (19). 1935
Six species of molds.	3-indol acetic acid	Ronsdorf (16). 1936
<i>Ph. tumefaciens</i>	Not identified	Brown and Gardner (3). 1936
Root nodule bacteria.	Not identified	Thimann (20). 1936

In a series of papers published between 1933 and 1935, Kögl and his co-workers (8, 9, 10) determined the chemical constitution of two plant hormones which they called auxins *a* and *b*. As a result of studies with these auxins, a third auxin, called *hetero-auxin*, was discovered in urine. Hetero-auxin was shown to be identical with 3-indol acetic acid (11). Since bacteriologists had

¹ Contribution from the department of botany.

known for many years that some microorganisms produce 3-indol acetic acid by oxidative deaminization of tryptophane, the identification of 3-indol acetic acid as an auxin made it quite apparent, in 1934, that the production of auxins by microorganisms is not uncommon.

Though it seems quite probable that a considerable number of species of microorganisms elaborate auxins, few species have actually been investigated. So far as we are aware, almost nothing is known of auxin production by those species of microorganisms numerically predominant in soil. Nevertheless, suggestions have been made that certain little-understood plant responses may be due to growth hormones produced in the soil by the action of microorganisms on organic matter. That auxin production in soil and at root surfaces might be of considerable significance to the plant can hardly be questioned.

Thus a need is indicated for a somewhat comprehensive survey of soil microorganisms to determine how commonly these are potential auxin producers. The present report is concerned with such a survey. Various attempts have been made to determine whether auxins are produced in soil under different conditions, and some attention has been given to the significance of auxins produced in soil, but these studies are incomplete and are not included in the present report.

METHODS

The cultures employed in this study were obtained from various Indiana soils. The bacteria and actinomycetes were isolated from dilution plates of sodium albuminate agar; and the molds, from peptone-glucose-acid agar. Microscopic examinations were made to insure the purity of each culture before it was used. No attempt was made to identify the various cultures.

The media used for cultivation of the microorganisms for auxin assays were beef extract-peptone agar and a synthetic medium containing a Frazier-Rupp (4) mineral base with glucose, asparagine, and ammonium sulfate. Duplicate plates of each medium were prepared for each culture. The plates were inoculated by streaking and were incubated at 30°C. under aerobic conditions. The beef extract-peptone agar plates were incubated for 12 days before being tested, and the plates containing the synthetic medium were incubated for 30 days before being tested. Solid media were preferred to liquid media because little auxin was produced in liquid media.

Auxin determinations were made by the *Avena* test essentially as recommended by Went and Thimann (21, p. 29) for water culture. Agar blocks approximately 10 mm. in volume were cut from the sterile agar immediately adjacent to the streaked culture and placed on *Avena* coleoptiles maintained at a temperature of 24°C. and at a humidity near saturation. Two auxin determinations were made on each of the duplicate plate cultures on each medium. The negative curvatures of the coleoptiles were determined by the use of a protractor such as that described by Went and Thimann (21, p. 33). No attempts were made to identify the auxins produced.

RESULTS

Auxin determinations, the results of which are presented in tables 2 and 3, are expressed as plant units contained in the 10-cmm. agar test block. According to Went and Thimann (21), a plant unit is that amount of auxin which, when applied in a 10-cmm. agar block to an *Avena* coleoptile, will

TABLE 2

Production of auxin from beef extract-peptone agar by various groups of soil microorganisms

ORGANISMS TESTED	NUMBER OF SPECIES TESTED	FREQUENCY DISTRIBUTION IN PERCENTAGE OF SPECIES TESTED PRODUCING INDICATED PLANT UNITS (P.U.) OF AUXIN*									AVER. P.U. PROD- UCED (ALL CUL- TURES)	AVER. P.U. PROD- UCED (POS- ITIVE CUL- TURES ONLY)
		0 p.u.	1-5 p.u.	6-10 p.u.	11-15 p.u.	16-20 p.u.	21-25 p.u.	26-30 p.u.	31-35 p.u.			
Bacteria												
Gram-negative rods.....	24	21	4	4	17	17	21	4	12	16	20	
Gram-positive rods.....	37	27	5	5	13	16	13	11	8	14	19	
Cocci.....	12	16	0	9	9	24	24	9	9	18	21	
Total bacteria.....	73	23	4	5	14	18	18	8	10	15	20	
Molds.....	39	54	0	11	20	8	5	3	0	6	14	
Actinomycetes.....	38	34	3	6	16	18	21	3	0	11	18	

* Plant units of auxin produced in a 10-cmm. agar test block.

TABLE 3

*Auxin production from mineral salts-asparagine-glucose-ammonium sulfate agar by various groups of soil microorganisms**

ORGANISM	P.U.†	ORGANISM	P.U.
Gram-positive R55	26	Gram-negative 54	21
40	14	11	31
R58	28	65	29
25	32	67a	18
16	15	45	16
30	10	216a	18
R69	20	44	18
33	16	Coccus 52a	17
58a	25	Actinomycetes 404	8
37	16	415	24
13	20		
53	9		

* Negative cultures omitted from the table.

† Plant units of auxin in a 10-cmm. agar test block.

cause 1° of curvature. Hence our figures representing plant units of auxin also represent the degrees of coleoptile curvature obtained in each case.

The results obtained by testing 150 species of Gram-positive and Gram-negative rods, cocci, molds, and actinomycetes on beef extract-peptone agar are presented in table 2. Ninety-nine, or approximately 66 per cent of the cul-

tures studied, were found to produce auxin from the substrate used. Seventy-seven per cent of the bacteria, 66 per cent of the actinomycetes, and 46 per cent of the molds tested were positive auxin producers, the average number of plant units produced by these positive bacteria, actinomycetes, and molds being 20, 18, and 14 respectively. Seventy-nine per cent of the Gram-negative rods, 73 per cent of the Gram-positive rods, and 83 per cent of the cocci produce auxin in approximately equal average concentrations.

One hundred cultures were streaked on the synthetic medium previously mentioned, but only 75 grew sufficiently well to warrant their being tested. Of these 75 species, 23 were Gram-positive rods, 11 Gram-negative rods, 4 cocci, 14 molds, and 23 actinomycetes. The species which were found capable of synthesizing auxin from the constituents of the synthetic medium are listed in table 3. It will be noted that 12 Gram-positive rods, 7 Gram-negative rods, 1 coccus, and 2 actinomycetes were able to synthesize auxin on the medium used. None of the molds tested is able to produce auxin from the synthetic medium. With one exception, all of the cultures which were able to produce auxin on the synthetic medium were also able to produce auxin from beef extract-peptone agar.

It might be expected that microorganisms would produce 3-indol acetic acid either as an intermediate or as an end product of the catabolism of tryptophane. Hence, the production of auxin by the action of microorganisms on organic materials containing tryptophane is expected. On the basis of known essential physiology of microorganisms, it would seem to be less expected that so high a proportion of the organisms should synthesize auxin from a relatively simple medium without tryptophane. The auxin appears actually to be synthesized and not to be the result of autolytic processes, since auxin has been detected in cultures in which almost all the cells subsequently sporulated, leaving little visible cell debris. The synthesis of auxins by numerous microorganisms, especially bacteria, strongly suggests that auxin may have a function in bacterial physiology. Presumably, some species of molds, bacteria, and actinomycetes do not produce auxins, although this is by no means certain. It is possible that under proper conditions and with sufficiently delicate experimental methods, some, if not all, of our negative cultures might be found to produce detectable concentrations of auxin.

Our results indicate that the soil flora is potentially capable of producing appreciable amounts of auxin in soils or elsewhere in nature where sufficient minerals or organic materials are present to support microbial growth.

SUMMARY

One hundred and fifty species of actinomycetes, bacteria, and molds from Indiana soils have been tested to determine their capacity to produce plant growth hormones from beef extract-peptone agar. Seventy-five of these species were also tested for auxin production from a synthetic medium without tryptophane. Sixty-six per cent of the species produced auxin on the organic medium; and 30 per cent, from the constituents of the synthetic medium.

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A REVISED METHOD FOR THE MICROSCOPIC EXAMINATION OF NATURAL STRUCTURE AND PORE SPACE IN SOILS

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Information concerning the natural structure and pore space in undisturbed samples of soil has been limited, because methods for making a microscopic examination of the soil profile were not devised until recently for this type of research.

Ross (4) has recommended a method for the preparation of thin sections of porous rocks by impregnation with Bakelite varnish diluted with a mixture of ether and methyl alcohol. The samples are submerged in a dilute solution of varnish to fill the pores and are dried at a temperature between 70° and 100°C. to remove the solvent and polymerize the varnish to form Bakelite. He also prepared sedimentary materials for microscopic study (5) by impregnation with Kollolith, which is a satisfactory cementing material because it can be melted easily, bubbles do not form when it solidifies, and when heated to 170°C. for several hours it remains clear and colorless. Kollolith is tougher than Canada balsam and can be readily polished with fine emery paper. Kubiena (2, p. 70-76) has also used this method in soil research. Leggette (3) found that a solution of Bakelite varnish and methyl alcohol containing a small amount of acetone will penetrate friable rock more rapidly than will a solution of Bakelite varnish in ether and alcohol. After a specimen is treated with the fixing solution, the solvent is volatilized by placing the specimen in a container under reduced pressure in order to hasten the rate of drying. Sideri (6) does not recommend the use of any cementing material for fine-textured soils which are compact and free from sand grains. Fir resin dissolved in xylene is used for friable samples. Harper and Volk (1) used lacquer in preparing thin sections of soil for microscopic examination. When soils contain large grains of quartz sand, grinding must proceed very carefully in order that the sand grains will not be disturbed. Lacquer is easily scratched when sand grains are dislodged, although it does not soften so quickly as Kollolith when subjected to rapid grinding. It is also difficult to prevent lacquer from forming bubbles when a flat, polished surface of a clod is attached to a glass slide; consequently, some other type of cementing material should be available for this purpose.

Since many different kinds of plastics can be obtained from commercial sources, an attempt was made to obtain as many of these materials as possible

and to determine which of these substances could be recommended for treating soil samples to be used for microscopic study or as a cement to attach prepared samples of soil to glass slides. The materials which were tested are listed in table 1.

Bakelite varnish was not only the best cementing material examined, but it can be used on all types of soil if the ratio of thinner to varnish is varied. Regular thinner, as furnished by the manufacturer, or methyl alcohol containing a small quantity of acetone, as used by Leggette (3), is satisfactory. One part of varnish and two parts of thinner should be used for most soils. If soils are porous the clod can be placed in the varnish for one or two hours, and a

TABLE 1

Source of material tested for value as a cement in the preparation of thin sections of soil for microscopic study

MATERIAL	SOURCE
Bakelite Lacquer No. 3128	Bakelite Corporation, New York, N. Y.
Bakelite Varnish No. 1305	Bakelite Corporation, Chicago, Ill.
Canada Balsam	Local
Clear Lacquer	Local
Durez	General Plastics, Inc., North Tonawanda, N. Y.
Kolloolith	Voigt & Hochgesang, Gottingen, Germany
Lauxite Resin	I. F. Laucks, Inc., Seattle, Wash.
Lucite	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
Plasto Resin No. 15	Advance Solvents & Chemical Corporation, New York, N. Y.
Resinel No. 3	Glyco Products Company, Brooklyn, N. Y.
Resoglaz	Advance Solvents & Chemical Corporation, New York, N. Y.
Sodium Silicate	Local
Tenite	Tennessee Eastman Corporation, Kingsport, Tenn.
Vinylite Resin "AYAT"	Carbide & Carbon Chemicals Corporation, New York, N. Y.
Vinylseal	Carbide & Carbon Chemicals Corporation, New York, N. Y.

satisfactory infiltration of the solution will occur. In order to obtain thorough penetration in fine-textured soils, the clod should be placed in an aluminum dish and covered with a dilute solution of Bakelite varnish. A partial vacuum should be created by placing the dish containing the soil in a desiccator which can be attached to a vacuum pump. When the vacuum is released, air pressure forces the solution into the soil pores if the clod is submerged in the liquid. Volatile material is removed by placing the treated soil in an oven at 60°C. for about one hour. This method of treatment keeps the varnish from forming bubbles as the solvent escapes. Several millimeters of surface soil should be removed by grinding in order to eliminate excessive concentrations of Bakelite, which may partially fill some of the noncapillary pore spaces.

Bakelite varnish is not satisfactory for use in cementing the polished surface of a clod to a glass slide, because it forms a dark semitransparent material when it hardens. Bakelite lacquer in thin layers is only very slightly colored, and it can be used to cement the surface of polished clods to glass slides so that thin sections can be prepared for microscopic study. Kollolith, Plasto Resin No. 15, and Resinel No. 3 are clear and colorless, but they are not so hard as an ideal cement should be. Soil can be treated with these resins by melting them and placing a small clod in the hot resin for 20 to 30 minutes. Evacuation of the air aids penetration in fine-textured soils when the partial vacuum is released. These resins can be used to cement the treated soil to glass slides if a small quantity of the material on the slide is melted by careful heating. In order to prevent rapid cooling of the resin, the soil should be heated in an oven before it is placed on the slide. This increases the depth of penetration of the resin into the noncapillary pore space in the soil. Other materials which were examined were too soft, too brittle, or too highly colored; would not bind the soil strongly enough to permit grinding; or affected the natural structure of the soil. A pronounced swelling occurred when Lucite was added to soils high in organic matter.

METHOD FOR THE PREPARATION OF THIN SECTIONS OF SOIL FOR MICROSCOPIC STUDY

Small clods of soil one-half to one inch in diameter should be collected from each horizon in a soil profile. If the soil is very loose, samples must be collected in metal containers, air dried, and treated with dilute lacquer solution to hold the soil together for additional treatment. Each sample should be marked so that the vertical or horizontal axis can be easily determined. Place the dry clod in an aluminum dish containing one part of Bakelite varnish diluted with two parts of Bakelite thinner. The clod should be submerged in the varnish. The solution will penetrate porous soils readily, but the air should be removed from fine-textured soils by placing the dish containing the soil and solution in a desiccator which can be attached to a vacuum pump, a mercury manometer being used to determine how much time is required to remove the air from the container. Leave the clod submerged in the Bakelite varnish for 15 minutes after the vacuum is released in order that the solution will penetrate into the fine pores of the soil. Transfer the clod to a small cardboard on which the soil number is marked, and dry in an oven at 60°C. for one hour to remove the solvent. Increase the temperature to 80°C. for one hour and finally to 100°C. for five or six hours. Remove the clod from the oven, cool, and prepare a smooth face by grinding on an emery wheel. A polished surface is prepared by rubbing the smooth face of the clod on No. 1, No. 0, and finally on No. 0000 emery paper. If some of the coarse particles of soil are removed during the grinding process, the sample can be given two treatments with Bakelite varnish or lacquer to develop a stronger bond between the soil particles. The surface of each clod must be well polished and

flat before it is cemented to the glass slide. Remove the dust from the pores in the polished surface of the clod, using air pressure if available. Place about six drops of Bakelite lacquer on a clean glass slide, and press the prepared surface of the specimen into the lacquer. Dry overnight at room temperature. Then dry in an oven at 60°C. for three or four hours and finally at 90°C. until the lacquer is very hard, which usually takes six or seven hours. The lacquer will turn brown if the temperature is higher than 90°C. for any length of time. If a resin is melted on the glass slide as a cementing material, heat the soil in an oven before it is forced into the hot liquid on the glass slide so that a deeper penetration of the resin into the soil pores will occur. Grind the specimen to any desired thickness, as previously described. Clean with air pressure or wash the thin section with 95 per cent ethyl alcohol to remove dust from the pores. The specimen is then ready for microscopic examination.

In many sandy soils, light will pass through the quartz grains, which will appear as pores when examined with a microscope not equipped with special prisms for mineral analysis or in a photograph. If, before the clod is cemented to the glass slide, the surface of glassy minerals is covered with black drawing ink to reduce the quantity of light passing through thin sections, satisfactory pictures can be obtained unless a high magnification is used. Under such conditions, the ink which enters the microcapillaries will shrink when it dries and will form very minute cracks. The black color also interferes with the study of such factors as organic matter distribution and iron cementation. Good photographs can be obtained only when an objective is used which will give a flat field. A 9- by 12-cm. camera with extension bellows equipped with a shutter and a Leitz 24-mm. objective can be used to obtain photographs of low magnification, a projection lantern being used as a source of reflected light. Place an opal glass beneath the slide and allow some light to pass through the slide to delineate the boundary of the noncapillary pore space.

Photographs of thin sections of soil taken at different depths in a Miller clay, an Enterprise very fine sandy loam, and a Portland clay loam profile are shown in plate 1. These soils were magnified 22 diameters when photographed but have been reduced to 4.5 diameters in the illustration. Miller clay has a high percentage of noncapillary pore space in the 6- to 12-inch layer. It is not difficult, therefore, to understand how granulation could occur as a result of the gradual separation of soil masses by root development. Below this depth the soil contains only a few small, round pores. Enterprise very fine sandy loam is porous throughout the entire profile. It contains many large fragments of minerals, chiefly quartz, which appear gray because the polished surface of the specimen was coated with black drawing ink to reduce the quantity of light passing through the minerals as compared with the large pore spaces. Portland clay loam has many large irregular-shaped pores throughout the entire profile. The organic matter content of this soil is high, and the cultivating effect of grass roots as they increase the quantity of macroscopic pore space is evident.

Noncapillary pore space in soils can be estimated by filling, with white casein paste,¹ the pores in a clod which has been hardened and polished. The surface of the soil is photographed by reflected light, and measurements can be made with a planimeter or similar measuring device. This method can be used to measure noncapillary pore space without grinding the soil to a thin section.

SUMMARY

A method has been described in which Bakelite varnish is used to cement soil particles together in order that clods of soil can be ground to thin sections for microscopic examination. Lacquer is satisfactory when soils do not contain grains of sand, which must be cemented firmly or they will be dislodged during the grinding process. Of fifteen different materials studied, only four were suitable for attaching the polished surface of a cemented clod to a glass slide. These substances are Bakelite lacquer, Kollolith, Plasto Resin No. 15, and Resinel No. 3. A method is proposed for the study and estimation of noncapillary pore space by filling the pores appearing in the polished face of a clod with white casein paste.

A study of undisturbed samples of soil under low and high magnification will give accurate information in regard to the character and amount of noncapillary pore space and other physical factors, such as soil granulation, distribution of soil concretions, and the dispersion of soil organic matter, which cannot be obtained by indirect methods of physical analysis.

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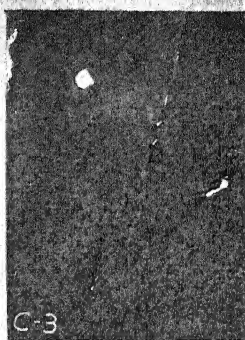
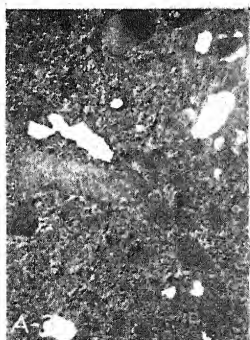
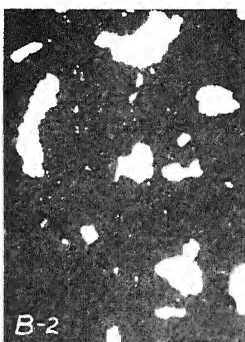
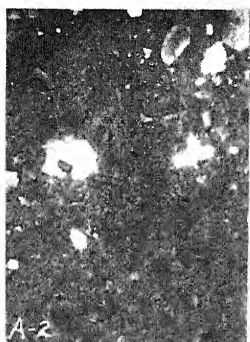
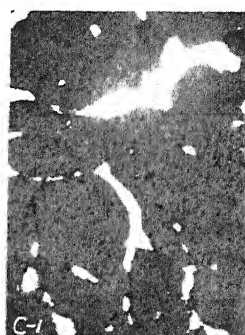
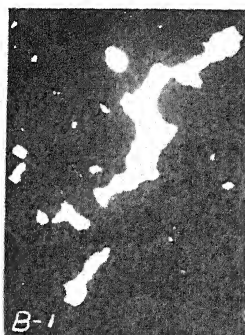
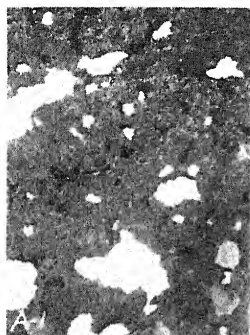
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¹ This material, the trade name of which is Texolite, is manufactured by the U. S. Gypsum Company, Chicago, Ill.

PLATE 1

NONCAPILLARY PORE SPACE IN SOIL PROFILES

(A) Enterprise very fine sandy loam, (B) Portland clay loam, (C) Miller clay. A-1, B-1 and C-1 represent a soil depth of 6 to 12 inches; A-2, B-2, and C-2, 18 to 24 inches; and A-3, B-3, and C-3, 30 to 36 inches. Magnification $\times 4.5$.



PHYSICAL CHARACTERISTICS OF SOILS: IV. DENSITY GRADIENTS IN SEDIMENTING COLUMNS AND A CHAIN-HYDROMETER FOR MECHANICAL ANALYSIS OF SOILS

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The use of the hydrometer for the mechanical analysis of soils has been popularized by Bouyoucos (1, 2, 3). The method has been criticized by Keen (4). To overcome some of the objections to the ordinary design, a new type of hydrometer was devised by the author (5). This hydrometer, which has a long thin stem and a short bulb, records density changes in a column 8-10 cm. long and situated 50-60 cm. from the top. The successful working of this hydrometer depends on the fact that the gradient of increasing density in the suspension of a sedimenting column becomes less and less steep as we go from top to bottom. In other words, the average density of a suspension, the length of which is small compared to the total depth of the sedimenting column, may be taken without serious error as the density of its middle point. The practical working of this type of hydrometer revealed two drawbacks, namely, the difficulty of making a long stem stand upright and the liability to breakage.

The hydrometer, though extensively used by road engineers, has never appealed to soil scientists as an instrument of precision which could replace the ordinary pipette method for the routine analysis of soils in the laboratory. The question is of importance, since an eminent soil physicist like Keen, while criticizing Bouyoucos' hydrometer method, has stated (4), "The determination was essentially qualitative since an appreciable density difference must exist in the suspension between top and bottom of the long hydrometer bulb after so short a period as 15 minutes." Further, he has stated, "Hence in physical terms, the hydrometer technique consists in measuring at an arbitrary time the average density of a layer of suspension several centimeters in length, whose density is continually changing both with depth and time. The statement that the method is 'essentially qualitative' is not a matter of personal opinion, but of fact." Keen has laid great stress on his main contention that the hydrometer method is essentially empirical and lacks the precision of theory and experiment associated with the science of pure physics.

One serious drawback in the hydrometer technic as compared to the pipette method lies in the fact that the former does not measure the concentration of particles at one point, but rather gives the average density of a fairly large section of the sedimenting column. This section, moreover, is not situated at a fixed distance from the top but moves with the changing concentrations of

the suspension, which affect the resting point of the hydrometer. The first defect is fundamental and cannot be removed unless a point hydrometer could be produced, or the concentration gradients in sedimenting columns could be examined and the magnitude of errors involved shown to be insignificant. The second defect could be removed by the use of a constant immersion chaino-hydrometer.

The object of this paper is to examine the uniformities of density gradients in the sedimenting columns of natural soils, leading to the development of a chaino-hydrometer of great sensitivity and precision.

DENSITY GRADIENTS IN SEDIMENTING COLUMNS

The basis of the hydrometer method is a single assumption; namely, the average density of any section of a sedimenting column is equal to the density at its middle point. Curiously, this assumption has never been subjected to a rigid test, though the general agreement between the hydrometer and the pipette method has been shown but has been ascribed largely to compensating errors assumed to have been operative in the majority of cases. This leaves the theoretical background unsound, and consequently the element of doubt has persisted.

Complete summation curves of 150 soils were determined by the pipette method. Ten-, fifteen-, and twenty-centimeter sections of the settling column, commencing from a depth 5 cm. from the surface, were considered as representing the lengths of the hydrometer bulb. The percentage of particles corresponding to each of several different settling times at the middle point of the section was determined by interpolation from the summation curves and calculated by taking the mean of percentages at the two extremities of this section. It was argued that if these two sets of values agreed among themselves, then the soundness of the assumption that the mean density equals the density at the middle of any section would be established. Further, the limiting length of the hydrometer bulb within which this relation holds, would also be known. For lack of space, the complete table recording these results is not given, but the following brief analysis of the results is equally convincing. The absolute differences between the percentage of particles calculated from the mean density and that determined directly at the middle point, for various sizes, are given in table 1 against the percentage of the total number of soils showing this difference.

It will be seen that in all cases the density gradient for any column below a depth of 5 cm. is symmetrical, and that, therefore, the density at its middle point is equal to the mean of the densities at the extremities. The differences increase as the bulb of the hydrometer is made longer, and only in the case of coarser fractions. For clay estimations the bulb may be as long as 20 cm. without introducing any appreciable error. We are, therefore, justified in taking the average density of any column and assuming it to be equal to the density at its middle point. This conclusion must set at rest any misgivings

regarding the use of the hydrometer for the mechanical analysis of soils and the acceptance of such results as truly representing the size distribution of particles.

It must be admitted that there is no theoretical reason why the density gradients of sections of sedimenting columns of soils should show such a uniformity, but there is also none why they should not, and therefore we must accept the facts as they are.

The results heretofore considered refer to soils completely dispersed by the $\text{Na}_2\text{CO}_3\text{-NaOH}$ method (6), but the relation is equally valid when the soils are subjected to no preliminary treatment for dispersion and are simply left in

TABLE 1

Comparison of percentages of particles calculated from the mean densities of sections of settling columns with those from densities at their middle points

LIMITING SIZES OF PARTI- CLES.....mm.	0.05			0.02			0.01			0.005			0.002		
	10	15*	20*	10	15	20	10	15	20	10	15	20	10	15	20
Length of hy- drometer bulb.....cm.	Percentage of soils														
Difference between percentages found by two methods															
10	0	2.1	4.2	0	0	0	0	0	0	0	0	0.7	0	0	0
9	0	2.1	2.1	0	0	0	0	0	0	0	0	0	0	0	0
8	0.7	0	2.1	0	0	0	0	0	0	0	0	0	0	0	0
7	0	0	4.2	0	0.7	2.0	0	0	0	0	0	0	0	0	0
6	0	2.1	2.1	0	0	0.7	0	0	2.7	0	0	1.3	0	0	0
5	0.7	4.2	6.3	0	2.6	3.3	0	0.7	1.3	0	0.7	1.3	0	0	0
4	0.7	6.3	2.1	0.7	2.1	6.7	0	0.7	4.0	0	2.0	2.7	0	0	0
3	2.0	10.4	10.4	3.3	8.7	17.3	0.7	3.3	7.3	0	3.3	3.3	0	0	2.1
2	12.6	16.7	22.9	14.0	24.6	22.7	4.0	17.3	24.7	4.6	9.3	16.7	0	0	0
1	39.3	31.3	25.0	36.6	36.7	30.7	22.0	44.0	34.0	21.3	30.7	30.7	0	0	14.6
0.5 and less	44.0	25.0	18.7	45.4	24.6	16.7	73.3	34.0	26.0	74.1	54.0	44.0	100.0	100.0	83.3

* 48 samples only, for each of these lengths, were analyzed for this size.

contact with water. Sixty undispersed soils were examined, and their summation percentage curves showed that the difference between the density at the middle point and the mean density for a 10-cm. section in no case exceeded 3.6 per cent reckoned in terms of absolute percentage of any fraction, and only two soils showed a difference of this order, and that too in the case of coarser fractions only; three soils showed a difference of 3 per cent, again in coarser fraction only; and all the rest gave a difference less than 2 per cent, the majority giving less than 1 per cent. This is a remarkable fact and one that enhances the value of the hydrometer method for determining the state of aggregation of compound particles in soils (7).

CHAINO-HYDROMETER

It is well known that measurements of weight can be made with far greater accuracy than can those of volume. It is for this reason that the analytical balance has never been surpassed for measuring densities of liquids and that the use of the hydrometer has been accepted as a rough-and-ready method only on account of the great saving in time. The chaino-hydrometer resulted from

HYDROMETER



CHAINOMETRIC ARRANGEMENT

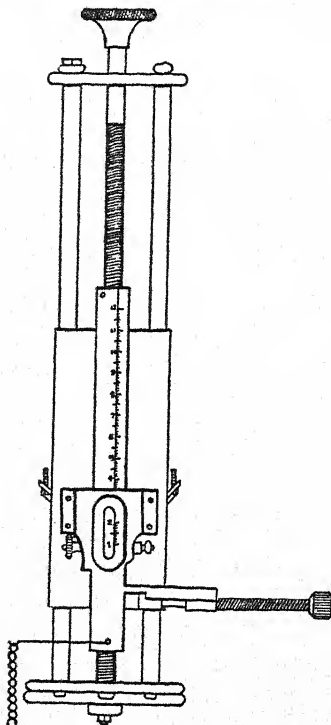


FIG. 1. THE CHAINO-HYDROMETER AND THE CHAINOMETRIC ARRANGEMENT

our attempt to combine the rapidity of the hydrometer and the precision of the analytical balance. It has proved to be an extremely sensitive instrument for measuring densities of liquids, especially soil suspensions.

The hydrometer, the principle of which is embodied in the well-known Nicholson's hydrometer, is shown in figure 1. It is made of brass and is chromium plated. The lower part of the stem of the hydrometer is shaped from a steel knitting needle, and the rectangular loop at the top is made of stout steel wire and carries a fine needle point. This needle point indicates

the limit to which the hydrometer is to be immersed. With this device, the immersion of the hydrometer can be reproduced to the fraction of a millimeter. In one corner of the loop is fixed an aluminum tube; and in the other, a hook. A fine chain 25 cm. long and weighing 0.5 gm. passes through the tube and, forming a loop, ends on the hook. The chain hangs from a hook which can be raised or lowered by a thumb screw working a vernier scale. A movement of 1.6 cm. on the scale corresponds to a change of 10 mgm. in the weight of the hydrometer. A total weight of 100 mgm. could be added by the chainometric arrangement. Larger weights are added directly on the special hooks in the center of the loop in continuation of the stem.

For uniformity of results, the chain must have a fixed initial loop when the vernier registers zero. This is accomplished by the help of another screw, shown at the top, which can move the whole chainometric arrangement. This is worked until a fixed number of chain rings or a fine mark on the chain has passed across a pointer. From this point onward the vernier scale is manipulated until the needle touches the surface of the liquid, when the hydrometer registers the true density of the suspension. It is important that the initial loop of the chain be made immediately before a reading is taken, and the final reading should always include a loop which is bigger than the initial loop.

We made some hydrometers from the bulbs of 100-cc. and 50-cc. pipettes by sealing both ends and attaching rectangular steel stems with sealing wax. If such a hydrometer breaks, a new one can be constructed, ready for use, within a few hours. The brass ones are, however, preferable. The glass hydrometers are weighted with mercury and the brass ones with lead shots.

TEMPERATURE CORRECTION

For a sensitive hydrometer, temperature correction is absolutely essential. This is calculated by weighing the hydrometer and taking into consideration the fact that the whole of that weight is lost when the hydrometer floats freely in water. The volume of the immersed portion of the hydrometer is obtained from the volume of an equal mass of water at that temperature. Knowing the coefficient of expansion of water with temperature, we can construct a table which will give at a glance the weight of the hydrometer at various temperatures. Thus if W is the weight of the hydrometer and W_t the additional weight added to bring it to the constant immersion point at temperature t we have:

$$W + W_t = V \times d_t$$

where V is the volume of the immersed portion of the hydrometer and d_t the density of water at $t^\circ\text{C}$. Thus, after one reading is taken at any temperature, the values of the additional weight at other temperatures are calculated from the known values of the density of water at these temperatures. In this relation we have assumed that V , the volume of the hydrometer, remains constant. Since the hydrometer is extremely sensitive, the results are affected

by the expansion or contraction of the material forming the bulb, and a positive or negative correction has to be applied when constructing the temperature correction chart.

If V_t is the volume of the hydrometer at temperature t , then its volume at any other temperature t' is given by the formula:

$$V_{t'} = V_t \{1 + \gamma (t' - t)\}$$

where γ is the coefficient of cubical expansion of the material forming the hydrometer. Thus the complete temperature correction chart can be constructed from the formula:

$$W + W_t = V_t \times d_t.$$

Thus one single weighing to find W and one single reading at any temperature t to find W_t suffices to construct the complete temperature correction chart. Actually the values of W_t are taken at three or four temperatures to check the calculated and found values. The values of W_t need not be calculated for fractions of a degree; this can be done for whole numbers, and the results plotted on an open scale from which the intermediate values for fractions of a degree are interpolated when preparing the temperature correction chart. Evidently the temperature correction chart gives the change in the density of water in terms of W_t . We also know that a change of density of 0.001 from that of water would produce a change of $0.001 \times V$ gm. in w where V is the volume of the hydrometer. Thus if the volume of the hydrometer is 100 cc. and if with the help of the chainometric arrangement w could be determined correct to a milligram, the densities could be found correct to the fifth decimal place. Actually an accuracy of this order is not necessary for the mechanical analysis of soils. The excess of density of 1 per cent soil suspension over water at the same temperature is 0.006269, assuming a density of 2.68 for the soil particles. This will produce a change of $0.006269 \times V$ gm. in the weight of the hydrometer. Thus the percentage of particles of any fraction in a 1 per cent suspension of soil is equal to

$$\frac{(w' - w) \times 100}{V \times 0.006269}$$

where w' is the additional weight at the constant immersion point and w is the weight of water at the same temperature (given in the temperature correction chart). As V is constant, the multiplying factor is calculated only once. Strictly speaking, V changes slightly with temperature, but this change is negligible for this purpose and need not be considered. It will be seen that if V is made equal to 159.5 cc., the multiplying factor becomes equal to 100, and $(w' - w)$ in milligrams gives directly the percentage of any fraction for a 1 per cent suspension. Alternately, if the concentration of the suspension is made equal to $\frac{159.5}{V}$, the factor will be 100.

A hydrometer may be tested occasionally at room temperature in distilled water, and if any change in the weight (w) is observed, a positive or negative correction is applied to all the values in the temperature calibration chart.

It is worthy of note that the hydrometer gives the density of the suspension, whereas the pipette method gives directly the percentage of suspended matter by weight. Agreement between the two methods can be expected only if the density of different soils is the same. We have assumed a density of 2.68 for all soils. This figure was obtained by actual measurements of density in a number of mineral soils; the average density was found to be 2.68, the lowest value being 2.64 and the highest 2.71. It might be mentioned that a difference of 0.04 in the actual density of the soil from the mean value will produce a difference of 1 per cent in the weight of the fraction. Since most of the mineral soils approximate the mean value, the difference between the hydrometer and the pipette method is not likely to be serious on this account.

TABLE 2

Comparison between the hydrometer and the pipette method for determining percentages of fractions

LIMITING SIZES OF PARTICLES.....mm.	0.02	0.01	0.005	0.002
Difference between percentages found by two methods	Number of soils			
4	3	1	1	0
3	3	2	2	0
2	10	7	9	4
1	13	19	22	12
0.5 and less	32	32	27	45

COMPARISON WITH THE PIPETTE METHOD

An important consideration that arises in the use of a hydrometer is the disturbance likely to be caused by the insertion of a large body in a settling column. How far this may affect the accuracy of results can be determined only by a direct comparison between the hydrometer and the pipette method. Sixty-one soils were analyzed by the two methods. The results are grouped in table 2. The absolute differences in the percentages of various fractions are given against the number of soils showing a difference of that order. The agreement is very good, in view of the fact that even in the pipette method a difference of the order of 2 in the percentage of any fraction is within the experimental error of the instrument.

REPRODUCIBILITY OF RESULTS

Reproducibility of results by the hydrometer method was compared with that by the pipette method. Fourteen soils were analyzed five times by both methods. The number of replicates for finer fractions was reduced to four, as accuracy is greater when the time of settling is long. To eliminate sampling

TABLE 3

Reproducibility of results with the hydrometer and the pipette method

LIMITING SIZE OF PARTICLES mm.		0.02			0.01			0.005		
Soil Number		Hydrometer 1	Hydrometer 2	Pipette	Hydrometer 1	Hydrometer 2	Pipette	Hydrometer 1	Hydrometer 2	Pipette
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
P.C. 13	Max.	79.21	80.99	80.25	70.43	72.45	72.30	64.92	64.20	66.20
	Min.	77.97	79.81	78.15	69.54	70.39	69.60	63.58	63.02	63.10
	Av.	78.31	80.16	78.91	69.95	71.33	70.50	64.33	63.69	64.25
P.C. 123	Max.	95.15	95.71	96.90	93.51	92.18	92.20	90.83	91.00	91.65
	Min.	94.40	95.12	92.85	92.17	91.30	89.90	89.94	88.35	89.70
	Av.	94.76	95.48	95.08	92.71	92.00	91.60	90.40	89.82	90.59
P.C. 166	Max.	77.73	75.39	74.30	70.73	68.91	69.25	62.54	60.67	59.15
	Min.	77.43	73.04	72.40	69.24	67.14	65.80	61.79	57.40	56.75
	Av.	77.58	74.10	73.69	69.86	68.09	67.00	62.17	58.82	58.11
R.M. 23	Max.	72.07	72.15	73.85	62.98	64.20	63.80	49.29	49.48	52.75
	Min.	71.62	71.56	71.00	61.64	62.14	61.05	48.84	47.12	48.35
	Av.	71.86	71.80	72.80	62.30	63.38	62.43	49.07	48.45	50.44
R.M. 24	Max.	87.26	88.06	88.20	77.58	77.75	80.17	62.69	62.43	64.15
	Min.	86.36	87.17	86.90	76.24	76.57	77.10	61.05	60.37	61.30
	Av.	86.84	87.59	87.54	76.89	77.16	78.17	61.87	61.48	62.74
R.M. 80	Max.	64.77	65.97	65.30	50.18	53.01	51.15	37.23	39.46	38.90
	Min.	62.24	63.32	64.50	48.84	48.59	48.95	36.18	37.11	36.95
	Av.	63.25	64.56	64.96	49.41	50.60	50.00	36.74	37.89	37.91
R.M. 88	Max.	46.31	48.89	48.25	37.23	38.29	37.60	27.84	28.27	29.00
	Min.	45.85	47.12	47.00	35.14	35.34	35.30	27.10	25.92	27.00
	Av.	46.10	47.59	47.61	36.13	36.64	36.67	27.40	26.73	27.80
R.M. 94	Max.	48.24	48.59	47.80	36.33	39.17	37.00	12.95	12.66	15.60
	Min.	46.61	47.12	46.25	34.21	37.40	35.70	12.21	11.78	13.65
	Av.	47.74	47.71	46.97	35.40	38.17	36.36	12.55	12.22	14.64
R.M. 96	Max.	80.85	83.93	84.05	67.15	69.21	66.25	49.43	50.01	52.10
	Min.	79.96	81.58	81.75	65.52	66.85	63.90	48.84	49.48	48.70
	Av.	80.50	82.81	82.86	66.35	67.97	65.32	49.17	49.63	50.44
R.M. 99	Max.	40.20	41.52	42.45	23.08	23.85	26.40	9.08	9.42	10.20
	Min.	38.71	40.05	40.60	21.59	22.97	23.00	8.19	8.25	8.25
	Av.	39.54	40.58	41.32	22.19	23.44	24.04	8.71	8.98	9.28
R.M. 100	Max.	11.17	12.66	12.45	10.13	11.19	10.60	9.68	7.66	10.05
	Min.	10.42	11.19	11.00	8.93	10.01	9.25	8.79	7.36	9.00
	Av.	10.75	11.72	11.62	9.53	10.60	9.76	9.31	7.51	9.76

TABLE 3—*Concluded*

LIMITING SIZE OF PARTICLES.....mm.		0.02			0.01			0.005		
Soil Number		Hydrometer 1	Hydrometer 2	Pipette	Hydrometer 1	Hydrometer 2	Pipette	Hydrometer 1	Hydrometer 2	Pipette
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
R.M. 104	Max.	40.20	41.23	41.40	30.23	30.34	30.90	21.89	21.50	22.80
	Min.	39.76	40.35	38.85	28.14	29.16	28.20	20.85	19.73	20.20
	Av.	39.99	40.76	39.78	29.04	29.75	29.38	21.37	20.76	21.93
R.M. 106	Max.	53.60	54.78	55.70	34.25	36.81	36.50	20.25	21.50	21.60
	Min.	52.12	53.01	54.00	32.76	35.34	35.90	19.21	20.32	20.15
	Av.	52.95	53.83	54.56	33.79	35.93	36.17	19.62	20.69	20.98
R.M. 115	Max.	29.78	30.33	30.75	22.34	23.27	21.35	15.63	15.31	15.60
	Min.	28.74	28.27	29.85	21.14	21.50	20.65	14.74	14.14	13.70
	Av.	29.39	29.45	30.28	21.89	22.21	21.01	15.15	14.65	14.69

Hydrometer 1: Length of bulb = 12.4 cm.; volume = 106.85 cc.

Hydrometer 2: Length of bulb = 10.8 cm.; volume = 54.00 cc.

errors, the same suspension was used for both methods. The results, given in table 3, show that the reproducibility of results is actually better with the hydrometer method than with the pipette method. These results also emphasize the close agreement between the hydrometer and the pipette method.

It might be pointed out that there is nothing arbitrary or empirical in the use of the chaino-hydrometer. The settling times of the particles of various sizes are calculated from Stokes' law to a depth corresponding to the middle point of the hydrometer bulb. If the bulb is not symmetrical about the middle point, then the mean density point corresponds to the center of gravity of the surface of the bulb and is calculated as follows:

The bulb is laid on graph paper with its axis horizontal, and its outline is then traced with a pencil held vertically. The resulting closed curve (fig. 2 a) forms a vertical projection of the surface of the bulb, and as the latter can be held to be generated by the revolution of either half of the curve about the line into which the axis projects, the following relation holds between the area A_1 of either half and the surface S of the bulb:

$$S = 2\pi \cdot A_1 \quad (1)$$

To find the coordinate of the center of gravity of the *surface* of the bulb, another curve (fig. 2 b) is drawn in which the coordinate is the product of the abscissa (x) of any point, as shown in fig. 2 a, and the corresponding ordinate (y). The area of this curve equals A_2 , where:

$$A_2 = \int_0^a xy \cdot dx \quad (2),$$

a being the length of the axis.

The abscissa of the center of gravity of the *surface* of the bulb then, according to the usual definition of the center of gravity, is given by

$$S \cdot \bar{x} = \int_0^a x \cdot 2\pi y \cdot dx \quad (3)$$

or

$$\begin{aligned} \bar{x} &= \frac{2\pi \int_0^a xy \cdot dx}{S} \\ &= \frac{2\pi A_2}{2\pi A_1} \quad \text{from (1) and (2)} \\ &= A_2/A_1. \end{aligned}$$

The ordinate of the center of gravity will be zero, since the bulb is symmetrical about the axis.

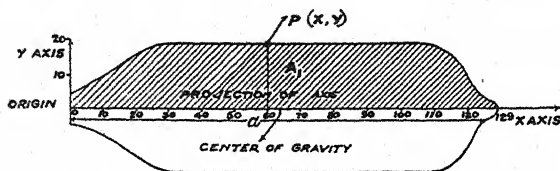


FIG. 2a

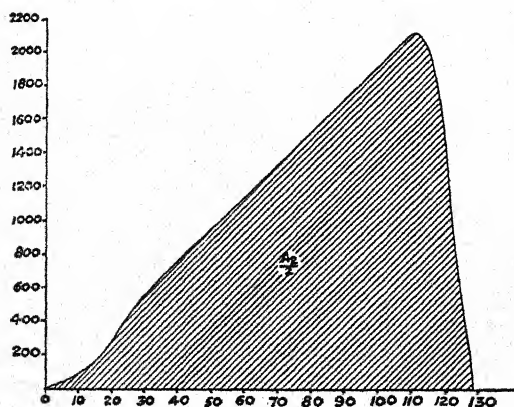


FIG. 2b

FIG. 2. METHOD OF CALCULATING THE MEAN DENSITY POINT OF THE HYDROMETER BULB

As the vertical scale of the ordinate in b is compressed to half, the area enclosed by the cube is one-half A_2 .

The hydrometer bulb, of course, can be made symmetrical, but we actually used hydrometers in which the bulbs were made from 100-cc. and 50-cc. pipettes. The mean density points were calculated in these cases, and pipet-

ting for comparison was done at these points. The object of introducing this discussion is to emphasize the fact that the *chaino-hydrometer does not lack the precision of theory and experiment associated with the science of pure physics*, a criticism offered by Keen for the hydrometer method in general. The hydrometer is lowered in the suspension just before the calculated settling time for the required size of particles to the depth corresponding to the middle point or the center of gravity of the bulb of the hydrometer, just as the pipette is lowered, in the pipette method. The disturbance caused is negligible, being no more than that in the pipette method. The hydrometer is not recommended for continuous readings by keeping it in the suspension and taking observations at definite intervals of time. Apart from the errors introduced by the actual settling of the particles on the bulb of the hydrometer, such a procedure would require a separate hydrometer for each suspension, and thus a number of soils could not be examined simultaneously without adding to the cost of equipment. The object of the chaino-hydrometer is to replace the pipette method with a technic that is simpler, quicker, and more accurate. We have mounted the chainometric arrangement on a robust stand that can slide between rails. The 1- or 2-liter cylinders containing the soil suspensions are arranged in a row, and the chainometric arrangement is brought behind each cylinder one after the other at the appropriate time.

After the rigid and exhaustive comparison of the two methods, the pipette method has been replaced by the hydrometer in this laboratory. We find that complete mechanical analysis of the soil can be made in the time formerly required for the determination of the clay fraction only by the pipette method. The saving effected is not only in time but in the cost of equipment for dishes and heaters, which is considerable.

SUMMARY

From an examination of the density gradients in suspensions of 150 soils, it is concluded that any section 10-12 cm. in length and situated 5 cm. below the surface of the settling column has an average density which is equal to the density at its middle point. This fact makes it possible to measure the density and hence the percentage of particles at any point in a settling column with a hydrometer. For this purpose, a chaino-hydrometer of high sensitivity with a chainometric attachment has been devised and its use for the mechanical analysis of soils discussed.

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SOLUBILIZATION AND MOVEMENT OF ORGANIC FORMS OF NITROGEN IN THE SOIL

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The occurrence of large fluctuations in the total nitrogen, ammonia, and nitrate contents of arable land has been recorded by Leather (20), Russell (27), Russell and Appleyard (29), Waynick (49), Waynick and Sharp (50), Lemmermann and Wichers (21), Clarke (8), Annett et al. (1), Smith (36), Thornton and associates (44, 45), Prescott and Piper (26), Batham and Nigam (5), Penman and Rountree (25), Bartholomew (4), Wilshaw (52), Sreenivasan and Subrahmanyam (40), and others. Prescott and Piper (26), Annett et al. (1), Sahasrabuddhe and co-workers (30-34), Wilshaw (52), and others have made attempts to correlate such fluctuations with seasonal variations and with other soil and cropping conditions. It has even been reported by Wilsdon and Ali (51), Annett et al. (1), Sahasrabuddhe and co-workers (30-34), Desai (11), Gerlach (14), Vandecaveye and Villanueva (46), Wilshaw (52), and others that under favorable conditions of moisture, temperature, aeration, and manuring, definite recuperation of nitrogen may proceed in soils.

In a recent communication, Sreenivasan and Subrahmanyam (41) have drawn attention to the effect, on such investigations, of certain external factors such as the normal variation in the composition of the soil from point to point in the field, uneven distribution of organic matter, erosion, silting, and movement of soluble nutrients.

It is generally believed that among the nitrogenous constituents of the soil, only the nitrates and, to a certain extent, ammonia are capable of movement from one stratum to another, as has been reported by Hall (15), Cook (9), Brown (7), Sahasrabuddhe and Gokhale (33), Shrikhande (35), and others. In the ordinary field soil, nitrates are present only in small quantities, and hence, their movement may not lead to any considerable change in the total nitrogen contents of different layers. Some evidence has been adduced by Sreenivasan and Subrahmanyam (43) to show that, in addition to the mineralized nitrogen, certain forms of organic nitrogen are also capable of movement through the soil and that this movement is influenced by the reaction of the soil and its soluble salt content. As further work on the nature and extent of such movement seemed desirable, the present inquiry was undertaken.

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EXPERIMENTAL

Solubilization of nitrogen during the decomposition of organic matter

The following preliminary experiments were carried out to determine the extent to which organic nitrogen is solubilized during the decomposition of complex nitrogenous materials in the soil. Finely powdered air-dry samples of rice straw (0.3 per cent nitrogen) and of pongam leaves (*Pongamia glabra*, 3.4 per cent nitrogen) and a commercial specimen of dried blood (12.3 per cent nitrogen) were mixed, in quantities corresponding to 25 mgm. N, with 100-gm. lots of a local virgin red loam soil, air dried, and passed through a 3-mm. sieve, and the mixtures maintained at 50 per cent saturation. With a view to finding out the peptizing effect, if any, of soluble salts, two more series were

TABLE 1

Changes in mineralized and total water- and salt-soluble nitrogen during the decomposition of organic matter in soil

Nitrogen in p.p.m. of soil

TREATMENT	AT START				AFTER 30 DAYS' DECOMPOSITION				AFTER 75 DAYS' DECOMPOSITION			
	Water extract		Saline extract		Water extract		Saline extract		Water extract		Saline extract	
	Mineralized N	Total N	Mineralized N	Total N	Mineralized N	Total N	Mineralized N	Total N	Mineralized N	Total N	Mineralized N	Total N
Soil alone (control).....	5	12	8	14	8	14	10	18	14	19	18	22
Soil + rice straw.	8	51	6	37	8	58	12	44	22	58	29	62
Soil + dried blood.....	16	58	21	62	109	151	142	174	107	154	145	177
Soil + pongam leaf.....	18	65	23	..	59	84	94	86	66	98	85	101
Soil + pongam leaf + NaCl..	18	55	95	105	81	112
Soil + pongam leaf + CaO..	15	55	23	56	82	106	96	104	78	90	89	98

started by mixing 200 mgm. each of sodium chloride and lime with 100-gm. lots of the soil before treatment with pongam leaves in the manner described above. The mixtures, in 250-cc. conical flasks, loosely plugged with cotton wool, were incubated at 30° and allowed to decompose. The contents of the flasks were examined at the start and at the end of 30 and 75 days' decomposition respectively for (a) mineralized ($\text{NH}_3 + \text{NO}_3$) nitrogen and (b) total water- or salt-soluble nitrogen. One set of mixtures during each sampling was extracted by shaking with 200 cc. of water for 90 minutes and filtered, and another set was extracted with a similar quantity of a 2 per cent aqueous solution of NaCl for the same period before filtering. The mineralized nitrogen in an aliquot of the filtrate was determined in each case by distillation with

magnesia and Devarda's alloy (2), and the total nitrogen in another aliquot was determined by the usual Kjeldahl method after preliminary reduction of nitrates (38). The results are given in table 1.

It may be seen (table 1) that with the progress of decomposition, appreciable amounts of organic nitrogen are peptized in the different samples. A part of this nitrogen undoubtedly is being rapidly mineralized while it is being solubilized, and consequently the quantities of water- and salt-extractable nitrogen present in the system at any one time are generally small. In the presence of lime, the water extract gives a lower figure for peptized nitrogen; this is perhaps only to be expected, since lime flocculates some of the organic nitrogen in solution. There is not much difference in the water-soluble nitrogen due to the presence of sodium chloride in the mixture. Likewise, the differences between corresponding values for water- and salt-soluble nitrogen are only slight. For mineralized nitrogen, the higher values obtained in the saline extract as compared with those in the water extract are due to the greater extraction of the adsorbed ammonia from the soil.

Effect of swamping the soil on the solubilization of nitrogen

With a view to observing the comparative rates of solubilization of organic nitrogen under arid and swamp soil conditions, some experiments were carried out in which 100-gm. lots of the soil were treated with different organic materials in quantities corresponding to 60 mgm. of nitrogen. The substances employed were dried blood, lantana leaf powder (*Lantana camara* Linn., 2.2 per cent nitrogen), and pongam seed cake (3.4 per cent nitrogen). In one set of experiments, the mixtures were kept as before at 50 per cent saturation capacity; in the other set, they were swamped with 100 cc. of water before being incubated at 30°. The changes in the different forms of water-soluble nitrogen and in total nitrogen were followed in each case for 2 months at intervals of 20 days from the start. Total nitrogen in the samples was determined according to the method outlined by Sreenivasan (37) and by Sreenivasan and Subrahmanyam (39); and ammonia, nitric, and total nitrogen in aliquots of the filtrates obtained after extraction of the soil suspensions with 200 cc. of water were all determined according to the methods of the A. O. A. C. (2). For total nitrogen determinations, nitrate was first reduced in alkaline medium (38). The water-soluble organic nitrogen is the difference between the total and the mineralized water-soluble nitrogen. The results are recorded in table 2.

The general observations in regard to the rates of decomposition of the different materials and the losses in total nitrogen are similar to those recorded by earlier workers (18, 41, 42).

It is well known that in the swamp soil, transformations of added organic nitrogen stop at the ammonia stage and that nitrification does not take place until the initial fermentation subsides and aerobic conditions are restored.

TABLE 2
Changes in water-soluble and total nitrogen under moist and swamp soil conditions
Nitrogen in p.p.m. of soil

TREATMENT	AT START				AFTER 20 DAYS' DECOMPOSITION				AFTER 40 DAYS' DECOMPOSITION				AFTER 60 DAYS' DECOMPOSITION			
	Water-soluble N			Total N	Water-soluble N			Total N	Water-soluble N			Total N	Water-soluble N			Total N
	NH ₄ -N	Nitric N	Organic N		NH ₄ -N	Nitric N	Organic N		NH ₄ -N	Nitric N	Organic N		NH ₄ -N	Nitric N	Organic N	
<i>Moist Series</i>																
Soil alone (control).....	7	9	27	575	9	18	30	578	7	18	12	545	7	22	6	540
Soil + dried blood.....	11	7	75	1,175	46	49	30	1,104	77	65	32	1,028	55	80	29	940
Soil + oil cake.....	7	7	87	1,179	37	15	51	1,132	62	31	9	1,059	47	49	9	994
Soil + lantana leaf.....	5	11	49	1,165	11	11	36	1,165	28	28	6	1,095	19	36	11	1,050
<i>Swamped Series</i>																
Soil alone (control).....	7	11	29	571	11	11	28	579	16	6	5	516	11	11	13	520
Soil + dried blood.....	11	7	86	1,168	29	14	43	1,084	69	12	44	997	60	44	37	886
Soil + oil cake.....	10	7	91	1,170	23	9	60	1,100	56	11	22	1,038	52	28	20	960
Soil + lantana leaf.....	9	10	50	1,162	7	11	40	1,140	9	15	12	1,060	11	26	15	1,013

TABLE 3
Effect of sodium chloride on changes in water-soluble and total nitrogen
Nitrogen in p.p.m. of soil

TREATMENT	OCTOBER 15, 1937 (AT START)				NOVEMBER 5, 1937				NOVEMBER 28, 1937				DECEMBER 18, 1937				JANUARY 6, 1938			
	Water-soluble N			Total N	Water-soluble N			Total N	Water-soluble N			Total N	Water-soluble N			Total N	Water-soluble N			Total N
	NH ₄ -N	Nitric N	Organic N		NH ₄ -N	Nitric N	Organic N		NH ₄ -N	Nitric N	Organic N		NH ₄ -N	Nitric N	Organic N		NH ₄ -N	Nitric N	Organic N	
Soil alone (control).....	6	9	17	575	5	12	24	576	4	9	28	557	11	11	43	548	13	6	37	532
Soil + NaCl.....	7	12	21	566	7	8	25	566	5	16	32	548	6	6	36	536	15	3	43	519
Soil + lantana leaf.....	9	6	58	1,181	13	12	48	1,194	12	19	49	1,175	16	70	120	1,160	6	57	104	1,100
Soil + lantana leaf + NaCl...	16	6	52	1,174	18	6	47	1,160	22	6	44	1,143	14	8	65	1,121	15	12	63	1,048
Soil + dried blood.....	16	9	67	1,186	115	22	151	1,093	61	134	229	1,049	48	155	244	998	34	84	177	960
Soil + dried blood + NaCl....	23	12	58	1,185	101	11	154	1,065	66	32	121	1,005	79	29	151	944	45	22	102	924

Consequently, most of the mineralized nitrogen, especially in the initial stages of decomposition, is present in the system as ammonia and is held adsorbed by the soil colloidal complex. Hence, the inorganic nitrogen and the total water-soluble nitrogen in the flooded series (table 2) are always much less than the corresponding values in the moist series where most of the mineralized nitrogen exists as the readily extractable nitrate. Although the total water-soluble nitrogen is less in the swamped series than in the moist series, it may be observed that the water-soluble organic nitrogen is in almost all instances more than that in the corresponding moist series. Again, since the losses in total nitrogen are more pronounced in the flooded series [cf. also Harrison and Aiyer (17, 18)], the percentage of the total nitrogen present in water-soluble organic forms will be even more in these cases.

Influence of sodium chloride on the dissolution of organic nitrogen in the soil

The presence of small amounts of sodium chloride in the soil does not lead to the peptization of appreciably larger quantities of organic nitrogen (table 1). The following further experiments on the effect of addition of sodium chloride in small amounts were carried out. A number of shallow glazed earthenware pots were filled with 2-kgm. lots of the sieved air-dry soil. Dried blood and lantana leaves in quantities corresponding to 60 mgm. of nitrogen for every 100 gm. of soil were thoroughly incorporated into the soil in the different pots, and the mixtures were allowed to decompose under field conditions after their moisture contents had been raised to about 30 per cent of the weight of the soil. A control series with untreated soil was included. In one set of pots, the soil was also mixed thoroughly with 4 gm. of sodium chloride per pot before the addition of the organic materials. The changes in the different forms of water-soluble nitrogen and in total nitrogen were then followed in aliquot samples, as before, at periodic intervals. Table 3 gives the results obtained.

It may be noted that the presence of sodium chloride results in significant differences in the rate and extent of decomposition as measured by the formation of mineralized and organic water-soluble nitrogen and the changes in total nitrogen. Thus, in the presence of salt, the mineralization of added organic matter is less than in its absence. In particular, nitrification is greatly hampered in these cases obviously because of the less open texture brought about by the sodium ion. This results in greater accumulation of ammonia, especially in the later stages; and the soil, being also rendered alkaline in character by the sodium ion, volatilization of the ammonia follows. A greater loss in total nitrogen is therefore observed in all the sodium chloride-treated series.

Sodium chloride was observed to peptize more of the organic matter, since the water extracts in such cases were always darker in color and, besides, gave higher figures for total carbon as estimated in a few cases by the method described by Bhaskaran et al. (6). But it would appear that with sodium chloride, more of the carbon than of the nitrogenous compounds were brought into solution. Hence, water-soluble organic nitrogen was never significantly

different in these series from the values obtained in the series without sodium chloride. This may also be due to the greater losses in total nitrogen in the saline than in the corresponding control series.

Distribution and movement of different forms of organic nitrogen in the soil

Although the lateral and downward movement of soluble nitrogenous fertilizers, particularly of ammonia and nitrates in the soil has been studied by a number of workers no information is yet available regarding the possible movement of the humic organic nitrogen of the soil under similar conditions. It was therefore thought desirable to study the nitrogen content of the soil organic matter at different depths and during the decomposition of organic matter added to the surface layers.

In the following experiments, a number of cylinders (10 inches in height by $3\frac{1}{2}$ inches in diameter) made of thick paraffined paper were filled to a height of 9 inches with soil. The cylinders were stood in glass dishes of slightly greater diameter, and additional stability was given to the soil columns thus obtained by placing them in rows in a wooden chest with a frame for each. The soil, which was the air-dried loam used in the earlier studies, was brought to a moisture content of 30 per cent before being poured into the cylinders. Five sets of treatments were given as follows: (I) Soil, unmanured, control; (II) Soil with top 2 inches (about 250 gm.) thoroughly admixed with pongam leaf powder, equivalent to 60 mgm. of nitrogen; (III) same as (II) but the entire soil was mixed with 0.3 per cent sodium chloride before incorporation of the organic matter in the surface 2 inches; (IV) and (V), same as (II) but the soil was previously adjusted to pH 8.0 and 4.6 respectively by addition of the necessary amounts of dilute alkali and acid respectively.

The cylinders of soil columns thus made could be easily cut at any depth or depths desired, by means of a sharp metal plate, preventing, thereby, any mixing of the soil with other layers. At the beginning of the experiment and at intervals of one month thereafter, one cylinder from each series was removed for analysis. The cylinders were cut at depths of 2, 4, and 6 inches from the top; thus, four samples from successive depths were obtained each time. These samples were analyzed separately for mineralized ($\text{NH}_3 + \text{NO}_3$) nitrogen, total nitrogen, and the different fractions of organic nitrogen according to the scheme of Page and his co-workers (23, 24). The results are given diagrammatically in figures 1 to 5.

Changes in mineralized nitrogen. In the control series, the figures for mineralized nitrogen remained rather steady throughout the period of experimentation, nor was there any appreciable change in the values at different depths. In the second series it was noted that with the progress of decomposition considerable mineralized nitrogen accumulated in the lower layers, especially to a depth of 6 inches. This is significant in view of the fact that the leaf material was mixed only with the first 2 inches of the soil; there is thus definite evidence of a downward movement of the inorganic nitrogen. In the third

series, in which the soil was mixed with sodium chloride before the organic matter was added to the surface 2-inch layer, mineralization was confined mostly to the surface soil. Downward movement was not much in evidence, the figures for the second and subsequent layers being about the same as those for the unmanured control soil (series I). It was observed that the soil in the third series had become somewhat sticky and, in consequence, was not quite permeable. Similar results were obtained in the fourth series where the green manure was allowed to decompose in the surface layer of soil previously

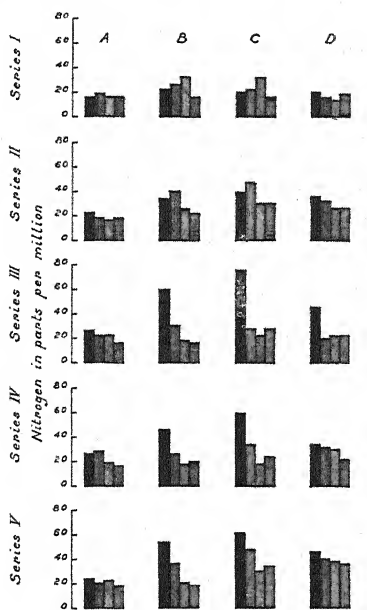


Fig. 1. Changes in mineralized nitrogen

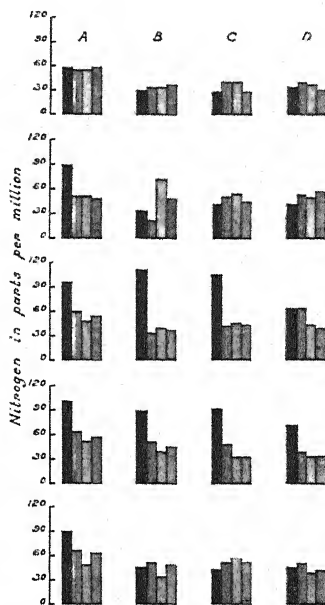


Fig. 2. Changes in hydrochloric acid-soluble nitrogen

- A) Sample taken at commencement. ■ 0 to 2 inches soil.
 B) " " after 1 month. ▒ 2 " 4 " "
 C) " " " 2 months. ▒ 4 " 6 " "
 D) " " " 4 " " 6 " 8 " "
- Series I to V represent treatments as given in text.

adjusted to pH 8, but mineralization was less rapid here, and percolation was slightly better. The low values for mineralized nitrogen even at the end of 4 months may also be due to some loss of ammonia due to the alkaline reaction of the soil. In the fifth series with soil adjusted to pH 4.6, ammonification in the surface layers was good. This was followed, as in series II, by a certain amount of movement of mineralized nitrogen into the lower layers.

Changes in hydrochloric acid-soluble nitrogen. In the control series, the values for HCl-soluble nitrogen fell rapidly during the first month as a result of conversion into other probably mineralized forms; the figures then remained nearly steady. In the manured series, there was a definite penetration of the

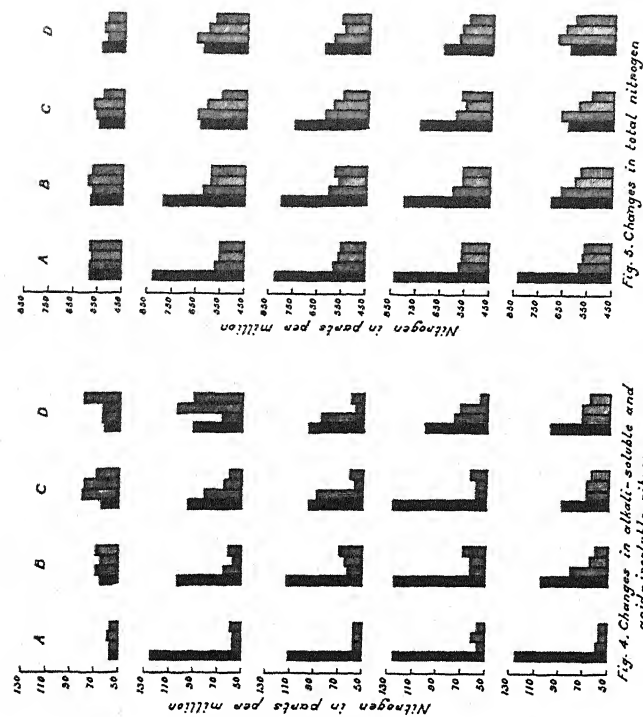
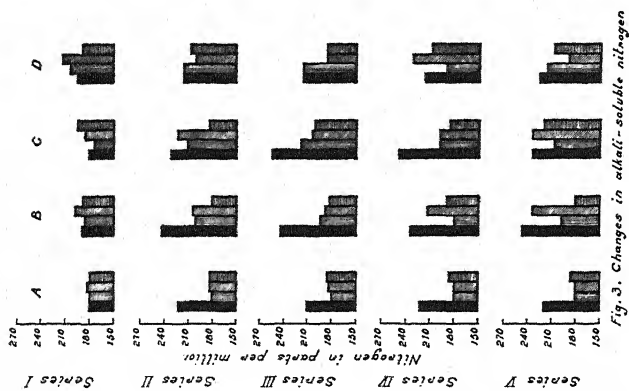


Fig. 5. Changes in total nitrogen

A) Sample taken at commencement.
B) 1 month.
C) 2 months.
D) 4 months.

Series I to V represent treatments as given in text.

acid-soluble nitrogen into the lower layers with the progress of decomposition. This form of nitrogen appeared to bear some relationship to the inorganic nitrogen in the different layers. In the saline soil, there was an accumulation in the surface layer during the first 2 months, followed by a slight movement to the lower layers. With the alkaline soil, more or less similar results were obtained, but no appreciable movement was evident. In the acid soil, the results were again similar to those in series II.

Changes in alkali-soluble nitrogen. Alkali-soluble nitrogen increased slightly with time even in the control series, probably because of fresh decomposing organic matter which the soil might have contained. In the manured series, there is, on the whole, an increase in alkali-soluble nitrogen. This is most pronounced in the first month of decomposition. Movement of alkali-soluble nitrogen from the surface to the lower layers is also definite and appreciable. The effects due to salt content of the soil or to changes in reaction are not very noticeable.

Changes in alkali-soluble and acid-insoluble nitrogen. In the unmanured control series, there was a slight increase, of about 20 per cent, in the value for alkali-soluble and acid-soluble nitrogen at the end of 4 months. The soil, taken from an uncultivated tract of land, obviously contained, at the time of sampling, some decomposing organic matter, which probably accounts for the observed increase in this form of nitrogen. In the manured series, a slight decrease in the surface soil was followed by a definite increase and downward movement. Similar results were obtained with the acid soil (series V). With the saline and alkaline soils (series III and IV), downward movement in this form of nitrogen was slight, penetration being confined, at best, to the first two layers.

Changes in total nitrogen. In the control soil, there was a slight loss in total nitrogen content at the end of 4 months; otherwise, the values remained nearly steady and were about the same in the different layers. In all the manured series, movement from the surface to the lower layers was evident. There was also a progressive loss in total nitrogen in these cases. In the saline and alkaline soils, the movement was less and the loss more than in the neutral and acid soils.

Changes in insoluble humin and in resistant nitrogen. The insoluble humin, of Page and co-workers (23, 24), was calculated for the four layers of the different series and at the various stages of decomposition by subtracting from the values for total nitrogen, the corresponding figures for acid- and alkali-soluble nitrogen. The values are given in table 4. Resistant nitrogen was determined independently in the soil samples according to the scheme of proximate analysis worked out by Waksman and Stevens (48). This represents the nitrogen in the residue after boiling with 5 per cent sulfuric acid for 6 hours [cf. also Duthie (12)]. The figures are included in table 4.

In the control series, the values for resistant nitrogen remain fairly steady in the topsoil and subsoil layers during the first 2 months, but at the end of 4

months, there is a fall in this constituent. In series II and V, a definite movement from the surface down to the subsoil layers is noted. In fact, the resistant nitrogen in the second or third layer of the soil is generally more than that in the surface 2 inches. It may be noted in this connection that Duthie (12) has also observed an increase in resistant protein of certain soil profiles with depth. With the saline and alkaline soils (series III and IV), however,

TABLE 4
Changes in "humin" and "resistant" nitrogen
Nitrogen in p.p.m. of soil

TREATMENT	DEPTH <i>inches</i>	JUNE 25, 1937		JULY 26, 1937		AUGUST 26, 1937		NOVEMBER 1, 1937	
		Humin N	Resistant N	Humin N	Resistant N	Humin N	Resistant N	Humin N	Resistant N
I. Control (untreated soil)	0-2	339	317	364	327	344	345	313	308
	2-4	339	319	350	305	344	352	279	287
	4-6	359	309	345	340	276	272
	6-9	344	324	301	360	301	274
II. Soil + green manure	0-2	513	362	508	346	365	329	368	306
	2-4	338	316	401	352	390	368	387	342
	4-6	315	362	331	310	359	320
	6-9	360	342	317	312	317	296
III. Soil + NaCl + green manure	0-2	515	375	461	364	389	325	355	296
	2-4	338	319	369	341	351	329	316	300
	4-6	332	307	342	329	321	296
	6-9	363	296	305	313	334	275
IV. Soil (pH 8.0) + green manure	0-2	509	477	410	355	401	379	359	326
	2-4	326	300	364	330	342	324	355	308
	4-6	318	336	319	307	312	208
	6-9	328	308	348	312	305	278
V. Soil (pH 4.6) + green manure	0-2	515	380	410	370	360	309	356	308
	2-4	328	348	409	364	404	371	410	362
	4-6	329	308	310	329	368	324
	6-9	353	302	268	275	314	279

there is a general fall in the values for resistant nitrogen toward the lower layers; such a decrease in resistant protein has been considered to indicate soil deterioration (12).

The changes in insoluble "humin" nitrogen and in resistant nitrogen did not appear to be related in any manner. There was a general decrease in "humin" nitrogen with the progress of decomposition in all cases, whereas the variation between different layers, even in the neutral and acid soils (series II and V), were irregular in many instances. On the other hand, the resistant nitrogen

did not change much as a result of progressive decomposition of the leaf material, and it appeared probable that this constituent measured a more definite form of nondecomposable organic nitrogen of the soil than did the "humins" nitrogen.

DISCUSSION

The results have shown that in the soil and during the decomposition of organic residues, there is appreciable solubilization of some forms of organic nitrogen, which may, under favorable conditions of texture and reaction, steadily move from one stratum to another. There have been numerous investigations on the study of the nature of the soil organic matter and of the relations between carbon and nitrogen in regard to the origin, nature, mode of formation, and fractionation of soil humic matter (47). Recent researches have also indicated that in temperate climates, the ratio of carbon to nitrogen diminishes significantly with depth of the soil within a profile (16, 22). In other words, there is a proportionately larger amount of nitrogenous complexes than of carbohydrate complexes present in the subsoil layers (12). Besides, Arnold and Page (3) find that the subsoil contains a type of humus which is more readily soluble in cold alkali than is the organic matter of the surface soil, and hence they conclude that the organic matter in the subsoil was not formed *in situ* as a result of decomposition, but was washed down from the surface soil. According to Crowther (10), nitrates and other nutrients in Rothamsted soils are stored to a considerable extent with the water in the subsoil structural units.

Russell (28) also observes that the soil reaction is an important factor determining accumulations of organic matter in the surface of soils or its mingling with the other layers. Earthworms are another important agency, especially in temperate and subtropical countries, in mixing up the soil constituents, dragging in leaves and other organic residues from the surface and thus facilitating decomposition by the microorganisms.

Although the solubilization and movement of organic nitrogen at any one time may be comparatively slight, yet, repeated action, especially during months of heavy and continuous rainfall, may carry down a considerable portion of the organic nitrogen to the lower strata of the soil. During dry weather, the decomposed organic residues of the subsoil may be carried up to the surface layers through capillary action. Such movements, as have been already pointed out by Sreenivasan and Subrahmanyam (43), may profoundly affect the nature and extent of fluctuations in the nitrogen contents of soils with seasonal variations. Their significance in relation to conservation and availability of soil nitrogen remains obscure. Mere surface analyses of soils in regard to supply of available nutrients will not be sufficient, therefore, for the evaluation of the fertility status of soils and may, indeed, often be misleading. Further work on the extent to which the plant draws upon the subsoil for its needs is therefore highly desirable.

SUMMARY

The changes in mineralized and total water-soluble nitrogen during the decomposition of organic materials such as dried blood, green manure, and seed cake in the soil have been followed. It is found that solubilization of organic forms of nitrogen is appreciable in the different cases. Lime flocculates a part of the organic nitrogen in solution.

The quantities of organic nitrogen brought into solution during the decomposition of organic matter in the soil are greater under swamp soil conditions than in moist soil. Under flooded conditions, there is also a greater loss in total nitrogen from the system, and hence the proportion of water-soluble or peptized organic nitrogen is even more in such cases.

In the presence of sodium chloride, increase in water-soluble organic nitrogen in the soil is slight, but loss of total nitrogen is more.

Study of the changes in mineralized and total nitrogen and in the different fractions of organic nitrogen through successive layers of soil of which only the surface 2 inches was mixed with green manure has revealed that, during decomposition, there is considerable movement of the different forms of nitrogen from one stratum to another. The extent of such movement, determined mainly by the texture and reaction of the soil, is less pronounced in saline and alkaline soils than in acid or neutral soils.

The significance of such movements in relation to the periodic fluctuations in soil nitrogen and to the supply of available nutrients from the subsoil, has been indicated.

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POSSIBLE LOSSES OF NITROGEN FROM ACID SOILS THROUGH THE DECOMPOSITION OF NITRITES

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It is generally accepted, as a result of extensive studies on nitrification,¹ that the organic nitrogen of the soil is converted by organisms first to ammonia, then to nitrites, and next to nitrates. Nitrites may be decomposed by denitrifying organisms with some evolution of free nitrogen. Temple (4) reported that nitrites were rapidly decomposed in an acid soil with formation of N_2O_3 , which was detected by its odor. Turtschin (5) has recently reported that acid soils react with nitrites, with consequent losses of nitrogen in the form of gaseous nitrogenous compounds. Many soils do not nitrify ammonium sulfate well without additions of calcium carbonate (2). The question arises as to whether this is really a failure to nitrify or whether nitrites are produced and then decomposed, with consequent loss of nitrogen. In the latter event, serious losses might occur in some soils. The work here presented is a study of this problem.

PRELIMINARY WORK

In the preliminary work, 36 soil samples were selected from seven different counties of Texas, representing a variety of soil types. They were acid to almost neutral in reaction, with pH values of 4.4 to 6.9. The soils were first tested to determine whether they decompose nitrites. The soil mixtures were prepared in duplicate, by the use of 100 gm. of soil, 10 cc. sodium nitrite solution containing 10 mgm. nitrogen (equal to 100 p.p.m.), and enough water to equal 50 per cent of the water capacity of the soil. Similar mixtures were prepared with the further addition of 1 gm. of calcium carbonate. They were incubated for 2, 4, and 8 days at 35°C. Portions equivalent to 20 gm. of dry soil were then taken and nitrates and nitrites determined by the usual method (1).

At the end of the period, the quantity of nitrates had increased, and the quantity of nitrites had decreased. The net losses of nitrogen were determined by subtracting the average amounts of nitrate and nitrite nitrogen found at the end of the incubation period from the amounts of nitrous nitrogen added to each culture plus the amounts of nitric nitrogen found in the original soil.

¹ Since Waksman (6) gives many references, a lengthy bibliography is not cited here.

When calcium carbonate was not added, the average loss of nitrogen was 47 p.p.m. (equal to 47 per cent of the nitrite nitrogen added) in the first 2 days,

TABLE 1

Loss of nitrogen in 8 days from soil containing 100 p.p.m. of nitrites, with and without calcium carbonate

Results in parts nitrogen per million of soil

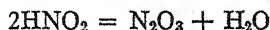
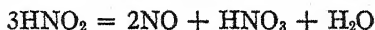
TYPE OF SOIL	DEPTH	pH OF ORIGINAL SOIL	LOSS OF NITROGEN	
			Without calcium carbonate	With 1 per cent calcium carbonate
	<i>inches</i>		<i>p.p.m.</i>	<i>p.p.m.</i>
Bowie fine sandy loam.....	7-10	5.4	84	4
Crockett fine sandy loam.....	7-19	6.0	91	8
Crockett very fine sandy loam.....	0-7	5.2	84	0
	7-13	4.7	55	31
Edna fine sandy loam.....	0-7	6.2	74	12
	7-19	6.1	70	12
Garner clay.....	0-7	5.4	86	48
	14-24	5.3	70	
Hockley fine sandy loam.....	0-7	6.4	65	1
	7-19	5.8	44	2
Hunt black clay.....	0-7	6.4	10	0
Kirvin fine sandy loam.....	7-19	4.4	72	8
Lake Charles clay.....	7-19	5.0	82	
	0-3	5.1	61	5
Leaf fine sandy loam.....	3-7	5.5	65	5
	15-19	4.7	65	30
Lufkin fine sandy loam.....	7-10	5.1	72	16
	7-19	4.9	66	25
Nacogdoches fine sandy loam.....	0-7	5.4	45	1
	7-19	5.2	63	1
Refugio loamy fine sand.....	0-7	6.9	34	0
	10-20	5.8	87	13
Ruston fine sandy loam.....	0-7	5.4	31	1
	7-19	5.2	62	0
Segno fine sandy loam.....	0-7	5.5	47	0
	7-19	4.6	72	0
Susquehanna fine sandy loam.....	7-18	5.3	75	6
	18-24	4.8	67	35
Susquehanna very fine sandy loam.....	0-12	5.9	76	7
Tabor fine sandy loam.....	0-7	5.1	68	3
	7-18	4.9	56	0
Wilson clay.....	19-36	4.5	63	21
	7-14	5.7	95	
Wilson clay loam.....	7-19	6.4	38	0
Wilson fine sandy loam.....	0-7	6.2	51	
Wilson very fine sandy loam.....	7-19	6.4	63	0

55 p.p.m. in 4 days, and 63 p.p.m. in 8 days. In about two-thirds of the tests lasting 2 days, from 15 to 44 p.p.m. of nitrate nitrogen was produced, probably by the decomposition of nitrous acid into NO and nitric acid as claimed by Turtshin, as 2 days was too short for appreciable nitrification to occur. Similar production of nitrates was obtained in the experiments made for 4 and for 8 days. The loss of nitrogen with some soils also appears to increase with length of the incubation period. The losses, however, are not proportional to the degree of acidity as indicated by the pH value of the soils. The net losses of nitrogen for each of the soils reacting 8 days are given in table 1.

When calcium carbonate was added, the average loss of nitrogen was 5 p.p.m. in 2 days, 8 p.p.m. in 4 days, and 9 p.p.m. in 8 days. Six of the soil samples lost over 20 per cent of the nitrite nitrogen in spite of the addition of calcium carbonate. The calcium carbonate added may not have been sufficient to neutralize the acidity or it may not have reacted with the acid soil particles during the short time of contact. This also is in agreement with the results of Turtshin. The results in table 1 show that nitrites may be retained in many soils without loss when they contain sufficient quantities of calcium carbonate.

POSSIBLE LOSSES OF NITRITE NITROGEN DURING NITRIFICATION OF AMMONIUM SULFATE IN ACID SOILS

Since the results of the foregoing experiment confirmed previous evidence that considerable losses of nitrogen may occur when nitrites are added to acid soils, it was thought necessary to ascertain whether losses occur in the nitrification of ammonium sulfate, as well as from sodium nitrite, for when the ammonia is converted to nitrites, these might possibly be decomposed in acid soils with loss of nitrogen. Turtshin (5) considered the decomposition to occur as follows:



Turtshin also claimed that the nitrous acid also combined to a small extent with the organic matter of the soil. These organic compounds probably undergo nitrification, with production of nitrates.

When calcium carbonate is added to some acid soils, all the ammonia added can eventually be recovered in the form of nitrates. If calcium carbonate is not first added to such acid soils, the ammonia added may be changed partly to nitrites, which, in turn, may be decomposed and part of the nitrogen lost. If calcium carbonate is added after this loss takes place, the quantities of nitrates then produced will be less than those produced when the calcium carbonate was added at the beginning of the experiment. This experiment would thus indicate whether or not there is a loss of nitrogen in the process of nitrification in acid soils which decompose nitrites chemically.

To test this possibility, 24 samples of acid soils were used. Four cultures were prepared from each soil, all receiving ammonium sulfate and all being inoculated with 10 cc. of a suspension of 20 gm. of actively nitrifying soil in 500 cc. of water, two of the four cultures also receiving an addition of calcium carbonate. All were then incubated at 35°C. After 28 days, each culture was emptied into a porcelain dish, mixed thoroughly with a spatula, and

TABLE 2
Effect of delayed application of calcium carbonate upon nitrification in acid soils
Results in parts nitrogen per million of soil

	DEPTH	N IN SOIL WITHOUT CALCIUM CARBONATE	N IN SOIL WITH CALCIUM CAR- BONATE ADDED		LOSS OF N
			At begin- ning†	After 28 days	
	<i>inches</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Crockett very fine sandy loam.....	0-7	135	493	556	0
	7-13	3	531	173	358
Garner clay.....	0-7	0	669	377	292
	14-24	0	550	139	411
Hunt black clay.....	0-7	294	669	631	38
Kirvin fine sandy loam.....	7-19	0	525	398	127
Lake Charles clay.....	7-19	0	613	277	336
Leaf fine sandy loam.....	0-3	135	456	513	0
	3-7	6	284	295	0
	15-19	3	556	199	357
Lufkin fine sandy loam.....	7-19	3	538	518	20
	7-10	0	488	433	55
Nacogdoches fine sandy loam.....	7-19	4	563	600	0
Refugio loamy fine sand.....	10-23	0	563	613	0
Segno fine sandy loam.....	18-24	0	513	556	0
Susquehanna fine sandy loam.....	7-18	3	425	538	0
	18-24	2	519	49	470
Tabor fine sandy loam.....	0-7	138	494	544	0
	7-18	66	481	538	0
	19-36	3	525	77	448
Wilson clay.....	7-14	0	619	688	0
Wilson clay loam.....	7-19	88	619	606	13
Wilson fine sandy loam.....	0-7	17	519	575	0
Wilson very fine sandy loam.....	7-19	35	544	544	0

calcium carbonate was added to the cultures which had not received calcium carbonate at the beginning of the experiment. All the cultures were returned to their beakers and incubated at 35°C. for 28 more days. Nitrates and nitrites were then determined as usual (1). The results of this work are given in table 2. In 16 of the 24 soil samples, the amount of nitrogen nitrified was virtually the same in the cultures to which the calcium carbonate was added at the beginning of the experiment as in the cultures to which it was

added after 28 days' incubation. There was no loss of nitrogen from these 16 soils. In the other eight soils, however, the amount of nitrogen recovered was much less in the cultures which received the addition of calcium carbonate after 28 days' incubation than in those which received the calcium carbonate at the beginning of the experiment. This indicated either loss of nitrogen or incomplete nitrification in those cultures.

It was thought possible that the low production of nitrates in the eight soils might have been due to the presence, at the end of the 28 days, when the calcium carbonate was added, of insufficient numbers of nitrifying organisms as a result of previous unfavorable conditions for growth. The experiment was accordingly repeated, with a second addition of inoculating liquid to all the cultures at the end of the first 28 days. The results of this experiment are given in table 3. There was no loss of nitrogen from most of the soils. With the excep-

TABLE 3

Effect of second inoculation on apparent loss of nitrogen from soil with delayed application of calcium carbonate

Results in parts nitrogen per million of soil

SOIL TYPE	DEPTH	N IN SOIL WITH CaCO ₃ ADDED		APPARENT LOSS OF N
		At beginning	After 28 days	
	<i>inches</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Crockett very fine sandy loam.....	7-13	563	619	0
Garner clay.....	0-7	638	588	50
	14-24	588	500	88
Kirvin fine sandy loam.....	7-19	538	525	13
Lake Charles clay.....	7-19	576	535	41
Leaf fine sandy loam.....	15-19	563	494	69
Susquehanna fine sandy loam.....	18-24	291	189	102
Tabor fine sandy loam.....	19-36	526	519	7

tion of Garner clay, these samples are all subsurface soils. The differences found in the previous experiment between most of the soils which received calcium carbonate at the beginning and those which did not, were thus due to an insufficient number of nitrifying organisms at the time of the second addition of calcium carbonate. But there were still differences in the quantities of nitrite and nitrate nitrogen in five of the eight soils, and these differences might be due to loss of nitrite nitrogen. The possible loss of nitrogen from Susquehanna fine sandy loam is 102 p.p.m., which is 20 per cent of the ammonia nitrogen added and over 33 per cent of the nitrite and nitrate nitrogen produced in the culture which received calcium carbonate at the beginning of the experiment. With the 14-24-inch layer of Garner clay, the possible loss is 88 p.p.m., or 17 per cent of the nitrogen added. With Leaf fine sandy loam, the possible loss is 69 p.p.m., or 14 per cent of the nitrogen added as ammonia.

With the surface layer of Garner clay, it is 50 p.p.m., or 10 per cent of the nitrogen added, and with Lake Charles clay, it is 41 p.p.m. or 8.2 per cent of the nitrogen added. These possible losses may, however, be due to the failure of the ammonia completely to nitrify in the cultures to which calcium carbonate was added after 28 days.

Another experiment, similar to the one described, was performed with four of the soils which apparently lost nitrogen. A sufficient supply of the other soil was not available. Ammonia nitrogen, as well as nitric and nitrate nitrogen, was determined. To determine ammonia nitrogen a portion from each culture equivalent to 50 gm. of dry soil was washed with 10 per cent potassium sulfate solution into a Kjeldahl flask. About 1 gm. of magnesium oxide was added with a pinch of zinc, and distillation was carried on with a low flame. The distillate was collected in 10 cc. of 0.2 *N* hydrochloric acid and then titrated with 0.1 *N* ammonium hydroxide. The results are given in table 4

TABLE 4
Effect on loss of nitrogen of calcium carbonate added at the beginning and after 28 days of incubation

	DEPTH	AT THE BEGINNING			AFTER 28 DAYS' INCUBATION			LOSS OF NITROGEN
		Nitric N	Ammonia N	Total N	Nitric N	Ammonia N	Total N	
		p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	
Garner clay.....	14-24	550	10	560	531	36	567	0
Lake Charles clay.....	7-19	575	14	589	481	157	638	0
Leaf fine sandy loam.....	15-19	550	7	557	575	10	585	0
Susquehanna fine sandy loam.....	18-24	424	85	509	69	343	412	97

No nitrites were found. There was no loss of nitrogen with three of the soils, but with Susquehanna fine sandy loam (subsurface), there was an apparent deficiency of 97 p.p.m. of nitrogen, nearly 20 per cent of the quantity added. This is larger than the limit of error and indicates a possibility of a loss of nitrogen. These samples were all heavy subsurface soils.

This experiment was again repeated, using subsurface layers of Lake Charles clay and Susquehanna fine sandy loam. Again there was no loss of nitrogen with Lake Charles clay, but some loss of nitrogen occurred with Susquehanna fine sandy loam. Thus it appears that there is no loss of nitrogen during the nitrification of ammonium sulfate in acid soils, except possibly in rare cases. Further investigation as to the occurrence of such soils is needed.

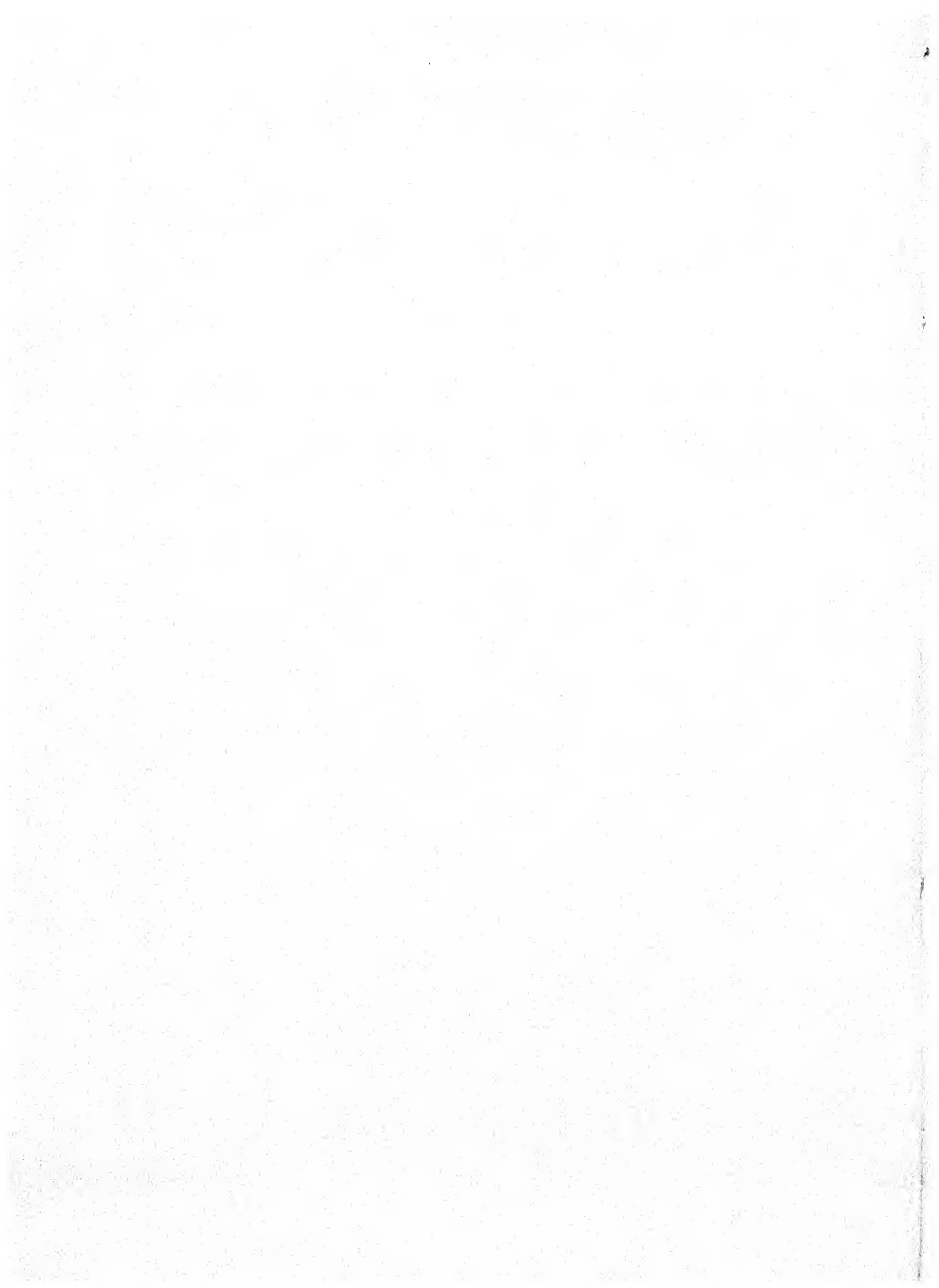
SUMMARY

Previous statements to the effect that nitrites are decomposed by acid soils are confirmed. There was no loss of nitrogen which could be ascribed to forma-

tion and decomposition of nitrites during the nitrification of ammonium sulfate in 23 of 24 soils which require additions of calcium carbonate for good nitrification. There was some loss with one of the subsurface soils, indicating that in rare cases nitrites may be formed during the nitrification of ammonium sulfate and decomposed chemically in acid soils with loss of nitrogen.

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PROPERTIES OF SOILS FROM NORTH AMERICAN ARCTIC REGIONS

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Soils of the far North, though of very minor importance insofar as agriculture is concerned, are of considerable interest as a means of extending our knowledge of the influence of the temperature and other factors which affect soil development on various kinds of parent rock.

The U. S. Department of Agriculture has, for a period of years, given considerable attention to relationships between the obvious characteristics used in the classification of soils and the chemical characteristics of the soils, particularly of their colloidal fractions. The materials collected for the present study, through the facilities of the Catholic University of America, have offered the first opportunity to examine soils, or, more exactly, materials exhibiting effects of incipient soil-forming processes, from arctic regions of northeastern North America.

One of the authors³, in annual visits to regions as far north as the outposts of human habitation, has collected much material of scientific interest. The Soil Chemistry and Physics Research Division felt that detailed examinations of some of the soil materials collected in these regions would be of considerable value. Such data would assist in the tracing northward of variations in soil characteristics to points beyond those previously considered in detail.

GENERAL CHARACTERISTICS OF ARCTIC SOILS

The influences of mechanical weathering forces, particularly those associated with freezing, thawing, and wind action, rather than those of the typical soil-forming processes of temperate zones, predominate in arctic regions. The sparse vegetation favors the activity of mechanical forces, since much of the surface is exposed except under snow cover. The soils of these regions are characterized by the presence of unweathered rocks and rock fragments, and in this respect they are comparable to the lithosols situated at the highest altitudes of mountains in more temperate regions. The normal soil-forming processes of eluviation and illuviation are greatly retarded under the frigid climatic conditions.

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The term "tundra" is often rather loosely applied to a wide range of highly organic soils of the vast treeless arctic regions and appears to have greater significance geographically or climatically than with reference to very definite soil formations. Nevertheless, certain general characteristics of tundra soils are recognized as being more or less typical (4, 11, 13, 15).

Under such conditions where profile development occurs, tundra soil formation appears to be related to the marsh type resulting from excessive moisture conditions (7, 11, 15); much of the soil surface is overlaid with peat or muck.

The region of North America, designated as tundra, embraces areas north of a line running roughly in a southeasterly direction from northern Alaska to the southern boundaries of Hudson Bay and including the northern and northeastern coastal areas of Labrador, according to a U. S. Department of Agriculture soil distribution map (12). A map prepared by Canadian authorities is in agreement with this general designation.⁴

Expeditions have been made by Russian and other scientists for the purpose of studying general conditions in the arctic. A very limited number of chemical and physical data regarding the arctic or tundra soils, however, is available. The general subject matter has been reviewed by Joffe (11), who notes the almost complete absence of definite information concerning soils of the arctic regions of North America with the exception of that found in the research of Canadian investigators (18, 20). The latter have dealt more specifically with geological formations and vegetation than with soils of the northern provinces of Canada. The work of Meinardus (13) summarizes the more important chemical and physical data of far northern soils which have been published by various authors. These data concern chiefly whole soils and parent rocks. Data for colloids or other soil fractions are apparently lacking.

The phenomenon of the perpetually frozen subsoil of vast areas of northern Asia has been described by Nikiforoff (16). This condition is known to exist also in the arctic regions of North America, although its exact extent is not known.

Arctic conditions frequently give rise to peculiar soil formations, among which are polygon fields. These are characterized by a network of cracks or fissures of remarkably uniform hexagonal or other shapes, as described by different writers (13, 17).

DESCRIPTION OF SAMPLES

The soils examined in this investigation were taken from widely separated areas ranging from a latitude of about 58° north at Churchill, Manitoba, to as far north as Craig Harbour, Ellesmere Island, in a latitude of about 76°. The expeditions beyond Churchill were made by boat, and the collections were necessarily made at points not very far from the seashore. The topography was, for the most part, moderately rough, barren rocks being exposed over

⁴ Privately communicated by G. N. Runke, Guelph, Ontario.

much of the area. The climate is extremely rigorous. The season when the temperature is high enough to permit thawing at the surface is very short, and hence the vegetation is sparse. This consists primarily of mosses, lichens, and a few stunted plants chiefly of the botanical families Salicaceae and Ericaceae. Certain species of willows 8 to 16 inches high are not uncommon at these northern outposts of vegetation. Organic residues do not readily decompose but tend, rather, to accumulate on the surface as peat or peatlike materials.

Soil profile development in these arctic regions is so markedly in its infancy that no appreciable differentiation into horizons was observed, at least in the areas of relatively rugged topography near the seashore from which most of the materials were collected. Hard rock was usually found so near the surface that no uniform depth of sampling or method of taking samples was practicable. Surface materials to a depth of 6 inches or less were usually collected for laboratory examination. Several of the samples were taken in small shallow depressions into which organic and inorganic materials had been washed from closely adjacent higher levels.

Thirty-seven samples were examined. The pH was determined by the hydrogen electrode on all the soil materials; mechanical analyses were made on 25, or on all except a few of very high organic matter content. Total ash, nitrogen, and organic carbon were determined on 14 samples of high and widely varying organic matter content. Total or partial analyses, depending upon the size of sample available, were made on the ash from ignition of six of the organic samples. The colloids were extracted from nine of the samples with clay contents of about 4 per cent or greater, and total analyses were made of each.

Brief descriptions of the samples, including geographical location and nature of the parent rocks and vegetation, are presented in table 1. The results of pH determinations, included in this table for the sake of convenience, show that most of the samples were acid and none were strongly alkaline.

The approximate locations of the samples and their distribution are indicated on the geological sketch map (fig. 1).

Photographs shown in plate 1 were taken in the regions where some of the samples were collected.

MECHANICAL COMPOSITION

To a considerable extent the mechanical composition of soil is influenced by climatic conditions. Certain relations have been pointed out between temperature and rainfall and the clay contents of soils (8, 10). High temperature and high rainfall tend toward the formation of clay soils except as eluviation processes remove the clay fractions from certain parts of the profiles to deposit this material in others. The low annual temperature together with moderate rainfall in most parts of the northern regions covered would be expected to result in very limited clay formation. This fact is brought out by the mechanical analyses of the samples as a whole, shown in table 2.

TABLE 1
Location and description of samples

SAMPLE NUMBER	LOCATION, LATITUDE, AND LONGITUDE	ELEVATION OR ALTITUDE <i>feet</i>	GENERAL DESCRIPTION*		GEOLOGICAL CLASSIFICATION AND PARENT ROCKS	VEGETATION	pH
			Material greater than 2 mm.	Material less than 2 mm.			
C3471	Churchill, Man., 58° 40' N., 94° 15' W.	100-150	(97%) Heterogeneous mixture of stream pebbles of granite, schists, and limestone (50%)	(3%) Inorganic fragments mixed with dark brown organic material. Good drainage	Silurian and Cambro-Silurian-Archaeon; Athabasca sandstone	Hedysarum, Vaccinium, mosses, lichens	6.7
C3472	Churchill, Man., 58° 40' N., 94° 15' W.	100-150	Nearly pure quartz fragments and sand	Small amount of black organic matter, origin probably from lichens. No drainage	Silurian and Cambro-Silurian-Archaeon; West Fort formation	Potentilla, Tyrola, lichens, Hedysarum; a few Salicaceae and Betulaceae	5.6
C3474	Chesterfield Inlet, N.W.T., 63° 25' N., 90° 40' W.	125-150	(98%) About 1/2 mica schist, 1/2 granite, 40% each of biotite and orthoclase, 20% quartz	(2%) Black organic matter a few inches deep, overlying granite. No drainage	Archaean	Ericaceae, Betulaceae. No Leguminosae	5.5
C3475	Wolstenholme, Que., 62° N., 77° W.	900-1,000	(36%) Well-weathered fragments of biotite and granite, rusty from decomposition. Order of attack probably feldspar, then biotite	(64%) Brown, light, friable material of sandy texture overlying granite. No drainage	Precambrian, unclassified (sediments, volcanics and intrusives)	Empetrum, Vaccinium, Arctostaphylos. No Leguminosae	4.2
C3476	Dorset, Baffin Island, N.W.T., 64° N., 76° W.	500-600	(36%) Almost entirely pink granite	(64%) Grayish friable sand. On a plateau. Poor or no drainage	Archaean and Precambrian (supposed) granite, gneiss	Oxytropis, Silene, Stellaria	4.7
C3478	Southampton Island, N.W.T., 63° N., 82° W.	100-150	(84%) Disintegrated pink and gray granite (50%), mixed with equal amount of fine-grained limestone, shell, and plant remains	(16%) Brown or dark brown organic fragments mixed with high proportion of sand. In an Arctic garden one year, virtually sterile	Silurian and Cambro-Silurian (west and south), Archaean (north and east)	Lichens, Saxifragaceae, Cruciferae	7.1
C3479	Wolstenholme, Que., 62° N., 77° W.	1,500	None	Brown, finely fibrous peat, with no mineral admixture, overlying granite. Surrounding rock devoid of soil	Precambrian, unclassified (sediments, volcanics and intrusives)	Grassy meadow; Poa, Alopecurus	4.2
C3480	Lake Harbour, N.W.T., 62° N., 70° W.	400-500	(16%) Angular pieces of quartz, about 85% silica, 10% feldspar, 5% mica, small amount buff sand. Covered with moss	(84%) Dark brown lumpy peaty material containing fine root-lets and sandy constituents	Archaean or Precambrian (supposed) granite, gneiss	Mixed heath, Carex, Oxytropis or Astragalus, mosses	5.7

C3481	Lake Harbour, N.W.T., 62° N., 70° W.	750	(36%) Decomposed buff granite, 50% feldspar, 25% quartz, little biotite mica. One piece of plagioclase feldspar. (41%) Disintegrated pink granite. Quartz 75%, feldspar 20%, hornblende 5%, slightly decomposed (30%) Weathered fragments of a biotite mica granite. Rusty color. Quartz 50%, orthoclase 40%, biotite 10% (61%) Angular pebbles of assorted crystallines as schists, quartzites, and pink and red granites. One small piece of limestone (1%) (12%) Pink hornblende talus with about 10% of marble (CaCO ₃) breccia	(64%) Similar in appearance to C3480 but contains a higher proportion of sandy constituents (59%) Brown, sandy material containing little organic matter with particles of lichens (70%) Brown or dark brown sand. Material overlying granite	Archaeon or Precambrian (supposed) granite, gneiss Archaeon or Precambrian (supposed) granite, gneiss Archaeon or Precambrian (supposed) granite, gneiss	Astragalus, Pyrola, Saxifragaceae	5.2
C3482	Lake Harbour, N.W.T., 62° N., 70° W.	400				Lichens, Ericaceae	5.4
C3483	Lake Harbour, N.W.T., 62° N., 70° W.	600				Lichens, Cruciferae	5.1
C3484	Pond's Inlet, N.W.T., 72° 50' N., 76° 40' W. Plateau at foot of an elevation 1000 feet	200-300			(39%) Gray sandy material, friable. Good drainage. Subsoil probably stream deposits	Very sparse; lichens and dead Salix	6.8
C3485	Craig Harbour, Ellesmere Island, N.W.T., 76° 20' N., 81° 30' W. At foot of a receding glacier	75-100			(88%) Gray sand. Good drainage. Subsoil of glacial deposit	Saxifragaceae and other seed plants	7.6
C3486	Craig Harbour, Ellesmere Island, N.W.T., 76° 20' N., 81° 30' W.	1,500	(55%) Essentially a quartz-feldspar aggregate. No limestone. Granite scrap 60%, gneiss 20% (21%) Quartz 30%, orthoclase 30%, hornblende 10%, garnet 10%. No mica. Decomposition only superficial	(45%) Light gray sandy material. Underlying stratum of granitic material. Good drainage (79%) Gray sandy material with low content of organic matter and clay. No drainage	Archaeon or Precambrian (supposed) granite Archaeon or Precambrian granite, gneiss (east), Lower Paleozoic (west)	Sparse; Carlamine, Draba, Saxifragaceae, and a few papaver Ericaceae, sedges, and grasses	6.3 5.1
C3488	Dundas, North Devon Island, N.W.T., 82° W. Southeast of H.B.C. post	450	(24%) Ferro-magnesian minerals (biotite and hornblende)	(76%) Gray, sandy, friable material with small contents of organic matter overlying granite. No drainage (61%) Red sandy loam. Subsoil is a colluvial debris. Poor drainage	Archaeon or Precambrian granite, gneiss (east), Lower Paleozoic (west)	Empetraceae, grasses, and sedges	5.7
C3489	Arctic Bay, Baffin Island, N.W.T., 73° N., 74° W. Southwest of H.B.C.	750	(39%) Weathered limestone. A few aggregates of well-crystallized quartz. Red color		Silurian and Cambrian-Silurian-Lower Paleozoic (noncoal bearing)	Vaccinium, Empetraceae, grasses, sedges	8.3
C3490	Arctic Bay, Baffin Island, N.W.T., 73° N., 74° W. On shallow depression in a large bare rock	200	(95%) About 75% tabular hydro-mica schist, with 15% quartzite and 10% granite scrap. No limestone.	(5%) Gray, dried organic material overlying powdery granite. No drainage	Silurian and Cambrian-Silurian-Lower Paleozoic (noncoal bearing)	No seed plants. Lichens	5.4

* Numbers in parentheses in each column represent percentages of total material fractionated by the 2-mm. mesh sieve.

TABLE 1—*Concluded*

SAMPLE NUMBER	LOCATION, LATITUDE, AND LONGITUDE	ELEVATION OR ALTITUDE <i>feet</i>	GENERAL DESCRIPTION*		GEOLOGICAL CLASSIFICATION AND PARENT ROCKS	VEGETATION	pH
			Material greater than 2 mm.	Material less than 2 mm.			
C3491	Arctic Bay, Baffin Island, N.W.T., 73° N., 74° W. Southeast of H.B.C. post; a mountain peak, 1800 feet altitude	300	None	Dark brown, finely fibrous peat, covered by a layer of dried moss. Considerable mineral material present. Deposit as much as 6 to 8 feet deep, resting on sandstone	Silurian and Cambro-Silurian-Lower Paleozoic (noncoal bearing)	Vaccinium, Empetrum	6.0
C3492	Clyde River, N.W.T., 70° N., 68° W. Northwest of H.B.C. post. On large isolated rock	100	(40%) Weathered, but still angular, fragments of biotite granite. No limestone	(60%) Grayish organic matter overlying granite. No drainage	Archaean and Precambrian (supposed) granite	Lichens, mosses, To-fieldia	5.3
C3493	Port Burwell, N.W.T., 60° N., 64° W.	50-100	None	Brown, finely fibrous peat, very little mineral admixture evident. Damp slope	Precambrian, unclassified (chiefly granite and granite-gneiss), Silurian (?)	Heavy vegetation; Ericaceae, grasses, sedges and mosses	5.8
C3494	Port Burwell, N.W.T., 60° N., 64° W. Southwest of H.B.C. post	100-150	(11%) Angular weathered gray biotite granite. Superficially pan-dried with sandy material. 50% feldspar, 30% quartz	(89%) Dark gray sandy loam, 6 to 8 inches deep, underlying stratum high in organic matter, resting on granite. Poor drainage		Sparse grasses, Vaccinium, Ericaceae	4.9
C3495	Port Burwell, N.W.T., 60° N., 64° W.	300	(7%) Slightly rounded pebbles, with powdered and sandy material; 10% limestone, 5% hematite	(93%) Polytonic sandy loam, oriented northwest. Thin layer of organic matter at 3-inch depth. Poor drainage		Naked surface but surrounded by Dryas, Vaccinium	7.6
C3496	Port Burwell, N.W.T., 60° N., 64° W. Near old Moravian mission	150-200	(11%) Crystalline metamorphics with a little sandy material. No organic matter. 75% pink granite, 10% blue granite	(89%) Dark brown clayey material overlying gneiss. No drainage		Lichens, Ericaceae	5.7
C3497	Port Burwell, N.W.T., 60° N., 64° W. At the foot of late snows	125-150	None	Brown sandy loam. Poor drainage		Sparse; Saxifragaceae, Draba	5.7
C3498	Dundas, North Devon Island, N.W.T., 74° N., 82° W.	400	None	Brown, lumpy peat or muck, with plant remains, fairly well decomposed. Some fine sand. Poor drainage	Archaean or Precambrian granite, gneiss (east), Lower Paleozoic (west)	Empetraceae, sedges, grasses	5.7

C3500	Wakeham Bay, Que., 62° N., 70° W.	500-600	(11%) Hornblende-biotite, schist with some quartzite and vein quartz; 25% feldspar, 15% hornblende, 10% biotite	(89%) Brown loamy sand material. Poor drainage	Precambrian, unclassified (sediments, volcanics, and intrusives), Archaean	Ericaceae, Cruciferae	4.9
C3502	Repulse Bay, N.W.T., 66° N., 86° W.	600	None	Dark brown loamy sand material. Poor drainage	Archaean gneiss, dykes of quartz, pegmatites, diabase	Lichens, mosses	4.6
C3503	Churchill, Man., 58° 40' N., 94° 15' W.	100-150	None	Light brown sphagnum and polytrichum moss peat, well preserved. No mineral admixture. Good drainage	Silurian and Cambro-Silurian-Archaean	None	3.8
C3504	Churchill, Man., 58° 40' N., 94° 15' W.	100-150	None	Light brown sphagnum moss peat, well preserved. No mineral admixture. Good drainage	Silurian and Cambro-Silurian-Archaean, West Fort	None	4.1
C3505	Churchill, Man., 58° 40' N., 94° 15' W.	100-150	None	Light brown to dark brown fibrous peat containing woody fragments and sphagnum moss, well preserved. Poor drainage	Silurian and Cambro-Silurian-Archaean, West Fort	Salicaceae	6.7
C3506	Churchill, Man., 58° 40' N., 94° 15' W.	100-150	(23%) Fossiliferous limestone, some of which is slightly sandy (quartzite); 90% CaCO ₃ , 10% SiO ₂	(77%) Dark brown fairly well decomposed, granular organic material. Admixture of light straw-colored fragments and sandy material	Silurian and Cambro-Silurian-Archaean, West Fort	Epilobium, Hedysarum	6.5
C3507	Churchill, Man., 58° 40' N., 94° 15' W.	100-150	(1%) Pyritiferous gray quartzite with a little admixture of pink granite; 90% SiO ₂	(99%) Brown coarse sandy material. Poor drainage	Silurian and Cambro-Silurian-Archaean, West Fort	Salicaceae, Astragalus	7.3
C3508	Churchill, Man., 58° 40' N., 94° 15' W.	100-150	(21%) About ½ twig-like woody material. Mineral matter containing about 60% limestone and 5% pyroclastic	(79%) Dark brown organic material with a considerable quantity of light, straw-colored undecomposed fragments	Silurian and Cambro-Silurian-Archaean, West Fort	Ericaceae	6.7
C3519	Letty Harbour, N.W.T., 69° N., 124° W.	200-300	(27%) Calcareous pebble bed; 70% limestone, 15% mica schist, 10% pink granite, 5% quartzite. All particles covered with CaCO ₃ dust	(73%) Light brown clay loam with little or no organic matter. Good drainage. Frozen subsoil	Paleozoic	Oxytropis	8.0
C3519A	Letty Harbour, N.W.T., 69° N., 124° W.	200-300	(6%) Calcareous rounded pebbles covered with CaCO ₃ dust 50%; quartz 20%; stony fragments	(94%) Brown silt loam. Subsoil frozen. Good drainage	Paleozoic	Oxytropis	8.0
C4354	Chateau Bay, Labrador		Lichen vegetation				

An outstanding feature of the data is the large amount of material falling in the larger size groups, such as gravel and coarse sand. Only three of the soils had as much as approximately 20 per cent clay, and nearly half of the soils had less than 5 per cent. In many cases, large quantities of the sample taken consisted of material greater than 2 mm. in diameter which was examined only to the extent noted in the descriptions of table 1.

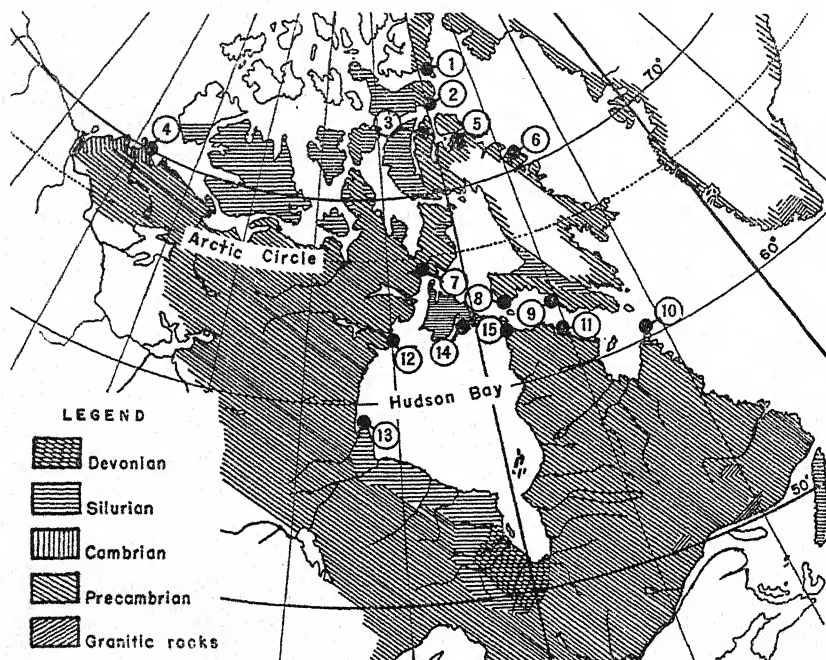


FIG. 1. SKETCH MAP OF NORTHEASTERN NORTH AMERICA, INDICATING GEOGRAPHICAL LOCATIONS OF THE SAMPLES COLLECTED

Key relating encircled numbers on map to laboratory numbers: 1, C3485-86; 2, C3487-88, C3498; 3, C3489-91; 4, C3519-19A; 5, C3484; 6, C3492; 7, C3502; 8, C3476; 9, C3480-83; 10, C3493-97; 11, C3500; 12, C3474; 13, C3471-72, C3503-08; 14, C3478; 15, C3475, C3479.

ORGANIC MATERIALS

Low-growing vegetation such as lichens, mosses, sedges, and heath shrubs, which have already been mentioned, are characteristic of the arctic under conditions where it is at all possible for them to become established. The growing season is extremely short, and consequently only a small annual addition is made to the supply of organic matter in the soil. The microbiological activity, however, is greatly reduced by the prevailing low temperatures, and the plant remains tend, therefore, to be readily preserved in the form of peat or in other forms of organic matter.

In some cases the organic materials had accumulated in small depressions

in the rocks, and in other cases vegetation had formed peat essentially in place. An admixture of considerable sand with the organic matter was frequently observed.

All of the samples having a high content of organic matter were analyzed for ash, carbon, and nitrogen with the object of obtaining characterizing data, particularly carbon-nitrogen ratios. These results are shown in table 3.

TABLE 2
*Mechanical analyses of soils from northeastern North America**

LABORATORY NUMBER	FIELD NUMBER	FINE GRAVEL 2-1 MM.	COARSE SAND 1-0.5 MM.	MEDIUM SAND 0.5-0.25 MM.	FINE SAND 0.25-0.1 MM.	VERY FINE SAND 0.1-0.05 MM.	SILT 0.05-0.002 MM.	CLAY <0.002 MM.	ORGANIC MATTER BY H ₂ O ₂	MINERAL MATTER DISSOLVED BY H ₂ O ₂
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
C3471	I	15.3	18.1	4.7	2.4	1.7	18.7	6.6	31.0	1.5
C3472	II	3.6	46.7	5.7	3.2	1.4	12.4	20.1	6.5	0.4
C3474	IV	22.5	34.9	10.6	13.0	4.0	4.2	2.3	7.7	0.8
C3475	V	21.3	25.7	15.1	20.4	5.5	7.8	1.9	2.0	0.3
C3476	VI	32.2	26.5	16.8	14.8	2.9	2.8	1.6	2.2	0.2
C3479	XI	13.2	39.9	14.6	11.3	3.1	4.6	2.2	10.5	0.6
C3482	XII	38.2	30.6	10.1	10.6	2.3	2.2	1.6	4.2	0.2
C3483	XIII	20.7	36.1	18.2	16.1	2.3	2.5	2.3	1.6	0.2
C3484	XIV	18.9	32.5	17.0	18.4	7.2	3.7	1.1	1.1	0.1
C3485	XV	7.5	23.1	17.4	29.4	12.6	6.8	2.2	0.7	0.3
C3486	XVI	28.1	24.0	11.5	16.6	9.0	5.6	1.1	3.6	0.5
C3487	XVII	9.8	12.3	7.4	19.7	17.6	28.3	1.1	3.5	0.3
C3488	XVIII	13.0	18.2	14.3	26.0	13.6	10.5	1.3	2.8	0.3
C3489	XIX	6.1	4.4	3.6	18.4	24.5	38.1	4.1	0.7	0.1
C3490	XX	5.5	7.8	4.4	9.8	8.4	36.8	19.4	7.4	0.5
C3492	XXII	25.8	26.1	11.8	14.9	6.0	6.9	3.9	4.3	0.3
C3494	XXIV	5.2	10.2	7.6	16.7	12.2	28.1	11.4	8.1	0.5
C3495	XXV	6.6	10.9	8.6	18.5	13.7	24.0	15.9	1.5	0.3
C3496	XXVI	12.6	13.8	8.2	16.6	15.0	28.4	3.7	1.5	0.2
C3497	XXVII	2.1	3.2	4.9	23.5	24.1	27.7	8.7	5.4	0.4
C3500	XL	7.8	14.4	16.8	28.5	17.2	11.2	1.6	2.3	0.2
C3502	XLI	24.1	25.9	9.7	10.0	2.4	11.4	3.5	12.4	0.6
C3507	330828-13	2.1	75.2	8.6	1.3	0.7	6.8	2.4	2.6	0.3
C3519	340816-26	2.4	2.3	2.1	7.3	11.8	45.5	27.1	1.1	0.4
C3519A	340816-25	2.1	2.4	2.5	7.4	18.2	56.7	7.9	2.4	0.4

* Mechanical analyses by T. M. Shaw and E. F. Miles.

A very wide range of carbon-nitrogen ratios is evident. This is not unusual, however, as variations of similar magnitude have been observed in analyses of peats or mucks collected in the United States (5, 6). In fact, the carbon-nitrogen ratios shown in table 3 are not greatly different from those of the American peats and mucks just referred to. The sample of sphagnum moss peat (No. C3504), for example, has the high ratio of 84.0, which is of the same order of magnitude as that corresponding to the same variety of peat collected

from various deposits of Maine (5). A number of the samples have carbon-nitrogen ratios around 16 to 18, which are characteristic of mucks and not greatly different from those of the organic matter of many soils in temperate climates (2). The carbon contents appear to be somewhat low when calculations are made on an ash-free basis, at least in the samples where the ash content was sufficiently low to justify confidence in the reliability of such calculations. The sphagnum moss peat samples have carbon contents of 45 and 46 per cent on the ash-free basis, whereas the Maine sphagnum peats previously analyzed had carbon contents of 50 per cent or higher. Carbon contents of other arctic peat samples ranged from 51 to 55 per cent, whereas percentages

TABLE 3

Partial analyses of peats or organic materials from northeastern North America

SAMPLE NUMBER	AIR-DRY MOISTURE	ASH CONTENT	NITROGEN*	CARBON*		CARBON NITROGEN RATIO
				Entire sample	Calculated on the ash- free basis†	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
C3471	5.81	58.03	1.32	24.14	21.3
C3478	2.42	81.63	0.54	8.75	18.9
C3479	9.25	26.21	2.79	38.82	52.61	16.2
C3480	8.25	50.78	1.67	26.80	18.7
C3481	3.56	70.44	1.03	16.25	18.4
C3491	6.10	63.53	1.28	20.31	18.5
C3493	9.90	35.85	2.40	34.26	53.41	16.7
C3498	7.53	57.69	1.38	21.91	18.5
C3503	9.83	4.89	0.98	43.95	46.21	52.3
C3504	9.27	3.20	0.61	43.96	45.41	84.0
C3505	9.17	37.30	1.52	32.34	51.58	24.8
C3506	6.46	58.88	1.31	21.52	19.2
C3508	5.31	60.84	1.11	20.61	21.7
C4354	9.34	3.17	1.85	34.70	35.83	21.9

* Determinations by J. H. Shimp and A. Yelmgren.

† Calculations were made only on samples containing less than 40 per cent ash.

of 55 to 60 were found to be common in peats in the United States referred to above.

The lichen sample (No. C4354) had an unusually low content of carbon, 34.70 per cent, as compared with that commonly found in fresh plant material. The average carbon content of a considerable variety of vegetation is approximately 45 per cent according to published data (19). Curiously, the nitrogen content of the lichens is relatively high, which accounts for the relatively low carbon-nitrogen ratio of 21.9. The latter value, however, is within the range of carbon-nitrogen ratios of 16 to 200 reported for fresh vegetation (9).

Since lichens are common in the arctic region, they have undoubtedly con-

tributed considerably to the various organic accumulations. Low carbon contents and low carbon-nitrogen ratios may, therefore, be expected in many cases.

ASH COMPOSITION

The ashes of the organic materials which had no significant admixture of extraneous mineral constituents and which were available in sufficient quantity were analyzed in detail as shown in table 4.

Only three of the samples selected for ash analyses (Nos. C3493, C3504, and C3505) can be considered as being peats. The others are perhaps more correctly termed mucks or peaty mucks, as indicated by their physical character and by the magnitude of the ash content.

It is of interest to compare the composition of the ash of the sphagnum peat (No. C3504) with that of the same variety of peat from Maine deposits pre-

TABLE 4
Chemical composition of the ash of peat or highly organic materials from northeastern North America*

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	SO ₃	IGNITION LOSS	TOTAL
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
C3491	39.96	0.43	11.11	4.10	0.14	15.30	9.66	1.79	0.98	0.59	0.63	15.57	100.26
C3493	55.93	0.40	14.88	12.81	0.40	6.38	2.97	1.79	1.71	0.91	1.72	0.74	100.64
C3498	52.89	0.48	17.34	12.95	0.22	7.22	1.77	2.79	2.23	0.64	0.64	1.69	100.86
C3504	65.53	0.16	8.58	1.84	0.08	10.69	1.78	1.87	1.71	0.43	1.70	6.54	100.91
C3505	71.94	0.60	11.94	3.14	0.05	2.78	1.68	3.23	0.08	0.92	2.14	1.68	100.18
C4354	35.37	0.73	19.19	8.99	0.22	3.41	5.22	13.43	2.46	9.74	Trace	0.84	99.60

* Chemical analyses by G. J. Hough.

viously published (5). The arctic sample of sphagnum peat is markedly higher in silica and potash but lower in sesquioxides, magnesium, and manganese, and much lower in phosphorus and sulfur. Other constituents, including calcium, are more or less similar. Taken as a whole, however, no striking differences were noted in the arctic samples as compared with samples from temperate regions. The contents of sulfur trioxide appear to be distinctly lower in the arctic samples, but insufficient data are at hand to warrant definite conclusions. The content of alumina is considerably greater than that of iron oxide, as has been similarly noted for peats of the United States (5).

The ash of the lichen is notably high in potash and phosphoric acid and is comparatively rich also in alumina, although to a less marked degree. The actual plant tissue, however, cannot be considered as rich in these constituents, since the total ash content was found to be only 3.17 per cent (see table 3).

In the process of ashing, considerable carbonates were formed. The tem-

perature used (about 550°C.) was not adequate actively to decompose these compounds. Hence the ashes show considerable and varying weight losses on ignition.

CHARACTER OF SOIL COLLOIDS

Certain features of the chemical composition of soil colloids give important indications regarding the dominant soil-making processes which have been operative, particularly when profile samples are considered. No data for soils or soil materials from temperate regions are available which closely approximate those here considered from northern latitudes. Samples from azonal soils of the lithosol group which are being developed on mountains essentially above the timber line would be expected to show some resemblance to those of the rough arctic areas. Chemical data for colloids of such soils in the United States are lacking, however. Comparisons with soil colloids of temperate regions, shown in table 5, are given only for the purpose of bringing out broad similarities and differences between the arctic materials and those of soils representative of groups that are well known. Data in various publications dealing with soils of the United States show, with important exceptions, that soils from regions of low rainfall, including the chernozems, tend to have colloids with ratios of silica to total bases ranging from about 5 to 8 (accompanying silica-alumina ratios are 4 or greater); the prairies about 8 to 10; the gray-brown podzolic group somewhat higher; and the red and yellow soils about 18 to 40. The silica-alumina ratios tend to vary inversely with those of silica to total bases. The very low ratios of silica to total bases of the arctic soil colloids together with values of intermediate magnitude for the silica-alumina ratios are indicative of only slight chemical alteration.

Two of the samples included in table 5, Nos. C3489 and C3495, are of particular interest.

Sample C3489 is a soil of distinctly red tint. This material is presumably the residuum from the decomposition and solution of limestone. No doubt the colloid obtained its distinctive characteristics in a former geological age, before the limestones were formed. For this reason the character of the colloid, indicated in part by its relatively low silica-sesquioxide ratio (1.92) does not necessarily reflect current arctic rock-weathering or soil-forming processes.

Sample C3495 is representative of the so-called polygonic soil areas frequently encountered in far northern regions on comparatively shallow clayey alluvial deposits. These are of striking appearance, as pointed out earlier in the text. The process of polygon formation is presumably directly related to a flooding or saturation of the soil with water followed by evaporation and a resultant contraction of the material. Freezing probably also exerts some influence. Table 5 presents the chemical composition of the colloidal fraction of a soil of this kind. The silica-alumina ratio is high but not quite so high as in one of the other samples. A factor of particular importance relative to the shrinkage behavior of this soil would seem to be the ratio silica to total bases,

TABLE 5
*Chemical analyses of the colloids of soils from northeastern North America**

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	SO ₃	IGNITION LOSS	TOTAL	SiO ₂ R ₂ O ₃	SiO ₂ Al ₂ O ₃	SiO ₂ TOTAL BASES
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent			
C3472	42.81	0.75	19.63	7.94	0.04	0.96	3.31	3.16	0.70	0.33	0.38	19.72	99.73	2.94	3.71	4.92
C3489	35.81	0.50	19.91	18.41	0.10	1.62	4.12	3.13	0.17	0.21	0.42	14.93	99.33	1.92	3.05	3.56
C3490	43.46	0.72	23.19	7.89	0.18	0.67	2.74	4.71	0.14	0.27	0.47	15.97	100.41	2.61	3.18	5.45
C3492	26.91	0.69	13.61	8.67	0.02	0.77	2.04	2.01	0.65	0.10	0.74	40.78	96.99†	2.34	3.35	4.64
C3494	31.77	0.76	15.96	12.33	0.19	0.96	3.17	2.29	0.44	0.56	0.58	31.02	100.03	2.26	3.38	4.14
C3495	42.70	0.84	20.26	11.76	0.18	1.88	4.64	3.46	1.03	0.28	0.22	13.44	100.69	2.62	3.58	3.51
C3497	30.55	0.77	15.79	12.30	0.04	0.94	2.81	1.93	0.44	0.56	0.82	32.56	99.51	2.18	3.28	4.44
C3519	45.52	0.60	23.69	9.30	0.09	1.15	4.17	4.57	0.29	0.13	0.11	10.34	99.96	2.61	3.26	4.26
C3519A	38.20	0.60	20.54	12.71	0.06	0.82	2.80	2.73	0.19	0.28	0.43	20.76	100.12	2.27	3.15	5.45

Colloids from three soils of the United States cited for comparison‡

Pima soil (3)	51.58	0.53	20.24	7.78	0.12	3.39	4.29	2.32	0.07	0.26	0.07	9.39	99.99	3.47	4.32	5.2
Shelby soil (14)	47.49	0.67	24.41	9.99	0.06	1.28	1.98	1.12	0.20	0.12	0.09	13.24	100.65	2.62	3.30	9.1
Davidson soil (1)	36.92	0.92	31.67	16.03	0.06	0.56	0.41	0.37	None	0.18	0.12	13.14	100.38	1.49	1.98	25.4

* Determinations by G. Edgington.

† Contains some copper and perhaps other bases not included in the analysis.

‡ From various publications of the U. S. Department of Agriculture.

which is the lowest found in the group. Perhaps of even greater importance is the sodium content (1.03 per cent Na_2O), which is the highest found in the group; in fact, much higher than is ordinarily found in nonsaline soils. It is well known that the presence of exchangeable sodium in soil colloids tends to increase their capacity for swelling and shrinkage. The high sodium content associated with a pH value as low as 7.6 excludes a possibility of the presence of more than traces of sodium carbonate. A test of the whole soil showed the presence of only about 0.04 per cent of total soluble salts, confirming their nonsaline character.

In view of the rather unusual chemical relations found in most of these colloids it seemed possible that they might differ somewhat crystallographically from those of the large number of colloids from temperate and tropical regions thus far examined. It seemed possible that slightly altered primary minerals might play a greater part. In the United States, soils the deep horizons of which are only moderately weathered, such as in those of the Miami series,

TABLE 6

Mineralogical composition of colloids shown by x-ray examinations and differential thermal analyses

SAMPLE NUMBER	HYDROUS MICA	KAOLINITE	GOETHITE AND HEMATITE
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
C3489	80	10	10
C3490	95	5	..
C3494	90	10	..
C3495	95	5	..
C3519	75	25	..
C3519A	80	20	..

show in their colloids the presence of clay minerals instead of fragments of such primary minerals as feldspars. In order to obtain evidence concerning the fate of primary minerals in soil colloid formation in the far northern latitudes, S. B. Hendricks, of the division of fertilizer research, Bureau of Chemistry and Soils, made x-ray examinations of six samples. His statement follows:

The separated colloids were examined by differential thermal analysis, and X-ray diffraction patterns were made from oriented and unoriented samples. The presence of organic matter seriously interfered with the heating curves and further caused trouble in obtaining oriented samples for X-ray work. For this reason and because oxides of iron were not removed before identification of the silicate minerals, the results given below [table 6] are not very accurate.⁵ The chief constituent in the various samples was hydrous mica, a mineral that is known by many names including illite and ordovician bentonite, intermixed with a minor amount of a kaolin mineral, probably kaolinite.

It is evident that minerals such as feldspars and hornblende, which are presumably present in the coarser granitic material, are not found in determinable

⁵ Quantities of samples available were inadequate for the conventional pretreatments.

quantities in the colloid even though these colloids in many ways show but little decomposition. The hydrous mica which predominates is a normal constituent of many soil colloids in considerable quantities.

The samples of soils, or in some cases more strictly soil materials, investigated in this report were collected from regions where typical tundra profiles might have been expected to be found. No evidence of well-defined profile characteristics was observed, however, in the limited areas examined. Since chemical analyses of the colloids of the typical tundra soils are not at hand, no comparison can be made of these with the present data. Such a comparison would furnish additional information relative to the influence of arctic conditions on soil formation. The samples may perhaps be logically classified for the most part as lithosol associates of what is recognized as true tundra. The general chemical character of the surface organic matter would be expected to be similar in both groups. The character of the parent rock, whether rugged and hard or comparatively soft and readily powdered, apparently plays an important role in determining the extent of profile development.

SUMMARY

A group of 37 soils and soil materials collected from the arctic region of northeastern North America were examined by the usual methods. The samples comprised both inorganic and predominately organic materials. Lack of profile development as well as certain chemical and physical characteristics is indicative of their extreme immaturity as soils.

Mechanical analyses of the samples examined showed that a large part of the materials consisted of particles in the coarser size groups. The clay content was generally small, only three of the samples having as much as approximately 20 per cent and a majority of the remainder having less than 5 per cent.

The wide range of carbon-nitrogen ratios in the organic materials was comparable to the variation found in peats and mucks of the United States. The carbon contents, calculated on an ash-free basis, however, appear to be somewhat lower than those of peat samples of this country.

Ash analyses indicated, on the whole, no striking differences, except perhaps for low contents of sulfur, as compared with ashes of peats and mucks from temperate regions.

Examinations of the colloids extracted from a group of the mineral soils show silica-base ratios of 5.5 or lower and accompanying silica-alumina ratios of 3.0 to 3.7. These and other factors are indicative of their extreme immaturity or of only a slight chemical alteration. Hydrous mica was shown by x-ray and heating curves to be the dominant clay mineral present.

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PLATE 1

SEVERAL LOCALITIES FROM WHICH SAMPLES WERE TAKEN FOR EXAMINATION

FIG. 1. Near Churchill, Man., location of sample C3472, showing lichens on rounded rocks and flowers blooming in the depression.

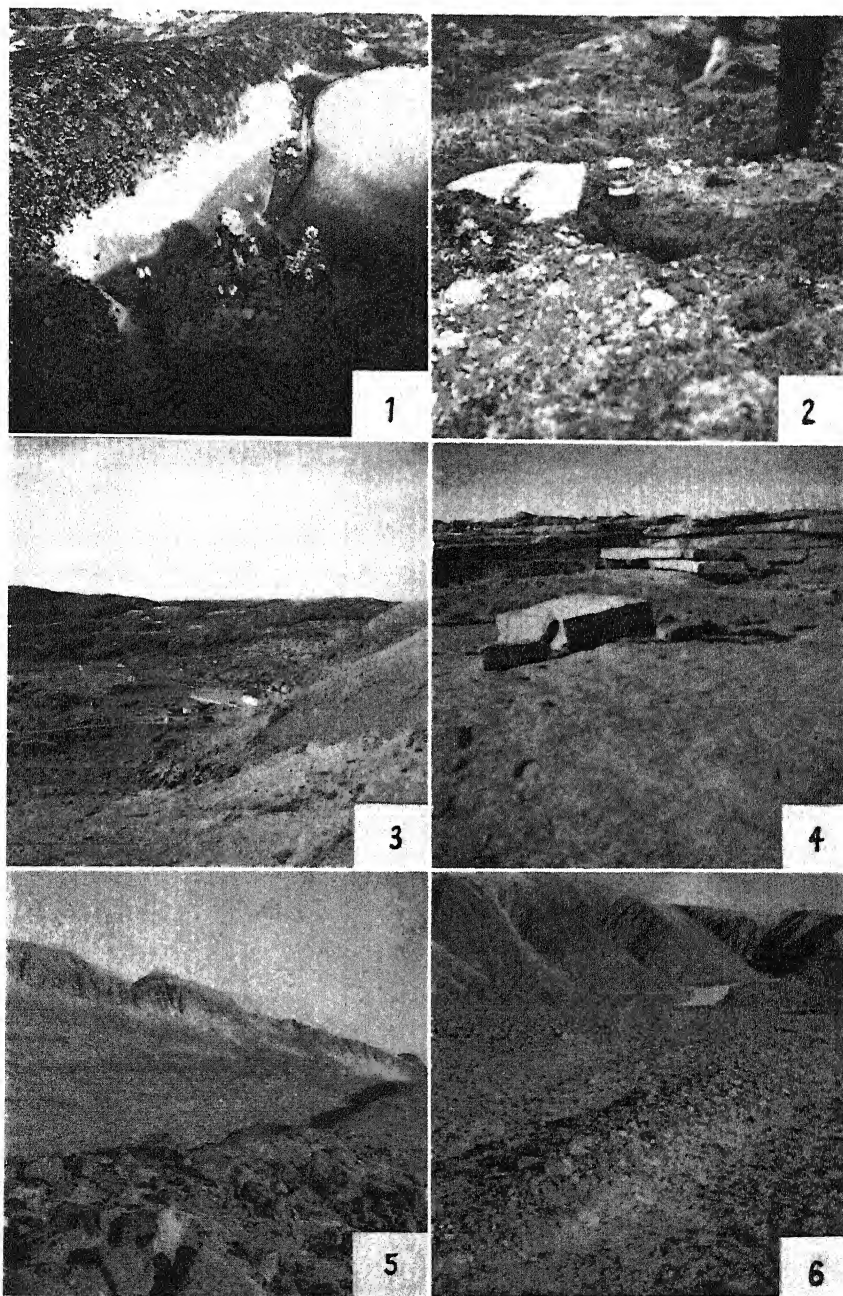
FIG. 2. Port Burwell, N.W.T., location of sample C3494. Sparse covering of grass.

FIG. 3. Lake Harbour, Baffin Island, N.W.T., near a Hudson Bay Company Post, location of samples C3480-83. Some heath vegetation is growing on mountain side in foreground.

FIG. 4. Fairway Island, N.W.T. Some vegetation can be seen near the background.

FIG. 5. Arctic Bay, Baffin Island, N.W.T. Sample C3490 was taken at the line of contact between rocks in foreground and ridge in background.

FIG. 6. Craig Harbour, Ellesmere Island, N.W.T., location of sample C3485. A receding glacier can be seen in the background.



FIGS. 1-6



THE COLLOIDAL CONSTITUENTS OF CALIFORNIA SOILS

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The importance of soil colloids is widely recognized. The permeability of soils to air and water, their adaptability to specific crops, their fertility, their absorptive power, and their tilth are all influenced to a marked degree by the colloidal constituents. For these reasons many soil scientists are actively engaged in research on soil colloids. Perhaps the most elementary questions that can be raised about soil colloids are these: (a) Of what specific substances are soil colloids composed, and (b) are the properties of soils due to the specific kinds of substances of which the colloids are composed, to the amount of colloidal material in the soil, or to the physical state of the colloidal materials? The following investigations were directed chiefly toward the first of these questions.

The classification of soils into types is based largely on clay content, and the clay fraction, as determined by mechanical analysis, commonly contains a large part of the colloids of the soil. This denotes, of course, that fine-textured soils contain higher percentages of colloid than do sandy types. As will be brought out later in this paper, the colloidal materials of different soil types are dissimilar, however, in certain important respects. For this and perhaps other reasons which will not be discussed in this paper, it is difficult to compare one type of clay, clay loam, or silt loam, with another. There is need for accurate knowledge concerning the colloidal constituents of the important soil types.

Formerly it was believed that the so-called clay of soils is amorphous and that the exchangeable ions are held on the surface of the colloidal particles by a vaguely defined force called "adsorption." It is now virtually certain, however, that neither of these ideas is entirely sound. Hendricks and Fry (17) and Kelley, Dore, and Brown (22) showed that the inorganic colloids of many different types of soils are largely crystalline. The results of Kelley and his co-workers (22, 23, 24) and of Marshall (28) strongly indicate that the exchangeable ions are lattice constituents. These facts have a mineralogical and geological as well as an agronomic interest. It is reasonable to expect that the discovery that the inorganic colloids of many types of soil are crystalline will lead ultimately to the complete identification of the more important components of soil colloids and to a clearer understanding of their fundamental properties.

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Hendricks and Fry concluded that the colloid of the Cecil series is related to halloysite and that several other soil types contain crystalline minerals which are more like the montmorillonite-beidellite clays. Allen (1) and Bray (5, 6) concluded that certain Illinois soils contain beidellite and nontronite. More recently Jacob et al. (20) and Kelley and Dore (21) reported three different types of clay minerals in soils.

It is possible that different types of clay minerals are formed in soils at different stages in the weathering process, or, more probably, that the leaching conditions exert an important influence on the kinds of clay minerals, both as regards their formation and occurrence. Noll (31) synthesized kaolinite and montmorillonite recently. He found that when Al_2O_3 and SiO_2 are heated together under pressure in the presence of H_2O , the temperature, the pH, and the concentration of certain bases present determine the kind of mineral that is formed. If Na, K, Ca, Mg, Cs, or Be is present in a certain range of concentration, montmorillonite, which is the chief mineral of the bentonitic clays, is formed. If NaOH is the only base present and in relatively high concentration, analcite is formed, which is a mineral related to the zeolites but is not a clay mineral. On the other hand, if the same mixture of Al_2O_3 and SiO_2 is heated under pressure in the presence of either pure H_2O or an aqueous solution of HCl, but in the total absence of bases, or when the concentration of bases is very low, kaolinite is formed. These results suggest that the kind and abundance of soluble bases present in the weathering materials and the pH of the medium may exert a significant influence on the type of clay mineral that is formed.

Noll's results suggest that the soils of arid and semiarid regions and the chernozem types of soils, which occur under intermediate rainfall, will be found to contain clay minerals of the montmorillonitic type, whereas the colloids of thoroughly leached soils will more likely resemble kaolinite. Partial confirmation of this idea has already been obtained (3). As will be shown in this paper, montmorillonite is not universally present, however, in semiarid soils; neither does it necessarily follow that montmorillonitic types of clay can be converted into kaolinite or halloysite merely by prolonged leaching, although a limited amount of evidence has been obtained (25) indicating that this conversion may take place in the state of nature.

Sedleckij (36) recently reported the synthesis of montmorillonite at ordinary temperature and atmospheric pressure. He first prepared an aluminosilicate gel by bringing together solutions of sodium silicate and sodium aluminate. The gel thus obtained was then leached with $N \text{ MgCl}_2$ until the pH of the leachate was 5.6. After virtually all the free chloride was leached out, the gel was held in a closed vessel at the temperature of the laboratory for about 4 years. Examination at the end of this period by x-ray, optical, and chemical methods showed that a crystalline product similar to montmorillonite had been formed. If this synthetic product was genuine montmorillonite, as its index of refraction suggests, then this is the first successful synthesis of a clay mineral under con-

ditions approaching those of atmospheric weathering. As will be more fully discussed in another paper, there is some doubt, however, about the mineralogical identity of this synthetic product.

METHOD OF SEPARATING THE COLLOID

The samples of colloids were separated from the coarser soil materials by the following method: About 1 kgm. of air-dried soil was dispersed in several liters of distilled water by vigorous shaking. To an occasional sample, a few drops of NH_4OH were added in order to bring about effective dispersion, but usually this was not necessary. After thorough agitation the suspensions were allowed to settle for 24 hours, then the upper 8 cm. was siphoned off. This process was repeated as many times as was necessary to obtain the desired amount of colloid. Assuming the applicability of Stokes' law to this type of material, the maximum diameter of the particles thus obtained would be approximately 1μ .

The colloidal suspensions thus obtained were coagulated with calcium chloride, and the clear supernatant liquid above the coagulated colloid was drawn off; additional amounts of calcium chloride solution were added, and the process was repeated several times. The coagulated colloidal material was then leached with distilled water until the greater part of the occluded calcium chloride was removed. Although most of the soils contained very little organic matter, the small amounts present in the colloids as separated were removed by prolonged oxidation with H_2O_2 at a temperature of approximately 80°C . After the oxidation was terminated, the samples were thoroughly leached with neutral, normal calcium acetate, then with methyl alcohol, and finally air dried. As thus prepared, the colloids were Ca-saturated. Their maximum content of carbon did not exceed 0.3 per cent, and most of the samples contained less than 0.1 per cent carbon. A special study showed that the treatment with calcium salts and H_2O_2 produced no important alteration in the clay minerals of these colloids.

With a few exceptions, all of the studies reported in this paper were made on the Ca-saturated forms of these colloids. The colloids, as separated, merely represent one fraction of the total colloid of these soils. It remains to be determined whether these samples were truly representative of the colloidal materials of these soils. The researches of Robinson and Holmes (33) and of Brown and Byers (8) suggest that the samples were fairly representative.

DESCRIPTION OF THE SOILS

The *Yolo* soils are alluvial, being derived from sandstones and shales with minor admixtures of material from other sources. They rarely contain CaCO_3 . These soils are relatively youthful, as shown by their profile characteristics. The following samples of *Yolo* were investigated:

Yolo silt loam, collected by C. F. Shaw from a grain field on the University Farm at Davis, *Yolo* County, California— No. 17557 (0-8 inches), No. 17558 (9-22 inches), No. 17559 (25-48 inches).

Yolo dark colored adobe clay, collected by S. W. Cosby from a virgin soil area $2\frac{1}{2}$ miles north of Gilroy, Santa Clara County, California—No. 7083 (0-8 inches).

Yolo light brown clay loam, collected by E. E. Thomas from an unirrigated grain field $\frac{1}{2}$ mile north of La Habra, Orange County, California—No. 431 (0-12 inches).

The *Vina* soils are alluvial and are derived from basic igneous rocks. In many cases the alluvium of the *Vina* soils has been eroded from Aiken soils areas, the Aiken being derived by residual weathering from basic igneous rocks. The *Vina* soils contain no CaCO_3 . They are recent or youthful soils, as shown by the absence of pronounced profile characteristics.

Vina loam, containing moderate amounts of organic matter, collected by W. W. Weir from an unirrigated grain field 2 miles south of Chico, Butte County, California—No. 16054 (0-12 inches), No. 16055 (12-40 inches).

Vina clay loam, collected by W. W. Weir from an unirrigated area 4 miles north of Chico, Butte County, California—No. 16056 (0-12 inches).

The *Keefers* soils are relatively mature and have been derived from old valley-filling basic igneous rock materials which were probably laid down as alluvial fans during Pleistocene times. This soil series is characterized by a fairly well developed profile free from CaCO_3 throughout and slightly acidic. The subsoil contains much more clay than does the surface soil. The *Keefers* is a comparatively unimportant soil series in California, only small areas having been mapped. It was included in this study because it represents an advanced stage in the weathering of soils derived from basic igneous rock materials under moderate rainfall (20-30 inches).

Keefers gravelly loam, collected by W. W. Weir 2 miles north of South Table Mountain and $8\frac{1}{2}$ miles east of Nelson, Butte County, California—No. 16057 (0-10 inches), No. 16058 (20-30 inches).

The *Sierra* soils are residual, being derived chiefly from granodiorites. As indicated by the physical characteristics of the profile, the soils of this series are fairly mature. The subsoil contains considerable accumulations of clay and in many localities rests directly on granite.

Sierra reddish brown sandy loam, collected by C. F. Shaw $\frac{1}{2}$ mile southwest of Mount Orcum, El Dorado County, California—No. 16308 ($\frac{1}{2}$ -8 inches), No. 16309 (11-20 inches), No. 16310 (22-28 inches), No. 16311 (33-43 inches).

The *Redding* soils are derived from alluvial deposits which are usually high in water-worn quartzose gravel and cobbles. The sediments are probably of Pleistocene age. This soil series is characterized by a mature profile which is definitely acidic throughout. The surface soil is reddish brown and of relatively low porosity. The B horizon is highly colloidal dense clay commonly containing many pebbles and cobbles. The B_2 horizon is, in some localities, a gray or mottled clay, as in samples 16307 and 16316. This series occurs in two distinctly different types of locality, namely, the northern part of the Sacramento Valley where the annual rainfall ranges from 20 to 30 inches, and near

San Diego where the annual rainfall is only 10 to 12 inches. Several profiles of this series were investigated.

Redding gravelly loam, collected by W. P. Kelley and S. M. Brown from an area of virgin soil on the Kearney Mesa, San Diego County, California—No. 16303 (1–15 inches), No. 16304 (20–30 inches), No. 16305 (4–18 inches), No. 16306 (18–20 inches), No. 16307 (20–37 inches).

Redding gravelly sandy loam, collected by C. F. Shaw from the S. W. $\frac{1}{4}$ Sec. 9, T 18 N, R 4 E, at Palermo, Butte County, California—No. 16314 (3–18 inches), No. 16315 (20–40 inches), No. 16316 (47–64 inches).

Redding gravelly sandy loam, collected by C. F. Shaw from the eastern part of Sec. 20, T 18 N, R 4 E, about 2 miles south of Palermo, Butte County, California, referred to hereafter as the Oroville profile—No. 16317 (2–17 inches), No. 16318 (17–40 inches).

Redding loam, collected by C. F. Shaw from the southwest corner, Sec. 14, T 20 N, R 5 W, $\frac{1}{2}$ mile north of Olinda, Shasta County, California—No. 16319 (3–17 inches), No. 16320 (17–34 inches), No. 16321 (34–66 inches).

The *San Joaquin* soils are derived mainly from arkosic sediments of Pleistocene age. This series is characterized by a dense, red hardpan 1 to 2 feet thick which occurs at a depth of from 20 to 40 inches. In the virgin state much of the soil of this series has a hummocky surface and is popularly known as "hog wallow" land. The San Joaquin series of soils occurs in various parts of the San Joaquin Valley where the rainfall is only 10 to 12 inches per annum. It also occurs in certain localities in southern California where the rainfall is less than 20 inches. Soils of this series have limited agricultural value because of the nearness to the surface of the dense impervious hardpan. Good yields of various kinds of crops are often obtained, however, on San Joaquin soils.

San Joaquin loam collected by R. E. Storie from virgin grassland in the Pixley area, 2 miles northwest of Hope Schoolhouse, Tulare County, California—No. 18882 (0–10 inches), No. 18883 (22–30 inches).

San Joaquin clay loam, collected by R. E. Storie from virgin grassland $1\frac{1}{2}$ miles south of Terra Bella, Tulare County, California—No. 18884 (0–12 inches), No. 18885 (24–32 inches).

San Joaquin sandy loam, collected by R. E. Storie from virgin grassland $1\frac{1}{2}$ miles west of Lindcove, Tulare County, California—No. 18888 (0–14 inches), No. 18889 (14–22 inches).

San Joaquin sandy loam, collected by C. F. Shaw from virgin grassland 1 mile south of Fairmead, Madera County, California—No. 6530 (0–10 inches).

The *Hanford* soils are developed from recently transported material derived from granitic sources. In many cases the alluvium has been eroded from areas of Holland or Sierra soils, both of which have been derived from granitic materials. The Hanford soils are youthful, showing but little evidence of segregation within the profile.

Hanford fine sandy loam, collected by C. F. Shaw $\frac{3}{4}$ mile southeast of Van Nuys in the San Fernando Valley, Los Angeles County, California—No. 7095 (0–8 inches).

Hanford sandy loam, collected by R. E. Storie from an unirrigated grain field 3 miles northeast of Delano, Kern County, California—No. 18886 (0–30 inches).

Hanford sandy loam collected by R. E. Storie from a virgin soil area 1 mile northwest of Exeter, Tulare County, California—No. 18887 (0–24 inches).

The *Ramona* soils are derived from alluvium eroded from Holland, Sierra, Vista, and Fallbrook soil areas, each of which was originally derived from granitic rocks. The *Ramona* series is characterized by a moderately mature profile; the subsoil contains more clay than the surface soil, and the lower part of the B horizon is usually a dense and rather compacted claypan.

Ramona loam, collected by C. F. Shaw from a grain field $\frac{1}{2}$ mile northeast of La Verne, Los Angeles County, California—No. 7091 (0-6 inches).

The *Placentia* soils are derived from granitic rocks and are similar to the *Ramona* soils in mode of occurrence, appearance of profile, and geological history, but are more mature. The B horizon is a dense and slowly pervious, compact claypan which, however, is not cemented or impervious to water, as is the hardpan of the San Joaquin series. *Placentia* soils are, therefore, less mature than San Joaquin soils.

Placentia loam, collected by C. F. Shaw from a grain field $2\frac{1}{2}$ miles northeast of La Verne, Los Angeles County, California—No. 7092 (0-6 inches).

The *Tujunga* soils consist of recent alluvium derived from granitic and other high-silica crystalline rocks. Soils of this series commonly contain many large stones and boulders of granite washed down from higher elevation along with the finer-grained materials. They are very immature soils, showing virtually no segregation within the profile.

Tujunga fine sandy loam, collected by C. F. Shaw from a geologically recent alluvial fan 1 mile southeast of Lankershim, Los Angeles County, California—No. 7094 (0-8 inches).

The *Madera* soils are derived from alluvium of mixed geological origin, but probably chiefly granodiorite. The granitic sediments were probably deposited in Pleistocene times, but subsequently more or less alluvium has been mixed with the older sediments, giving to this series a somewhat mixed origin. It occurs under an annual rainfall of 10 to 15 inches. The profile is usually mature. The subsoil is more dense than the surface soil and rests on a well-developed red hardpan which is usually slightly calcareous. This hardpan is less dense than that characterizing the San Joaquin series.

Madera clay loam, collected by C. F. Shaw from a virgin area in Sec. 15, T 85, R 15 E, near Madera, Madera County, California—No. 6528 (0-10 inches).

The *Tule* soils occur on the high terraces along the Tule River in Tulare County, California. Apparently derived from relatively old sediments of granitic origin, they are similar to the soils of the Redding series except that the pH is usually higher. In the soil survey report of this area, soon to be issued, the *Tule* soils will be shown as members of the Redding series. The surface of the *Tule* soils is characterized by a hummocky, hog wallow undulation suggestive of that of the San Joaquin soils. The subsoil is comparatively heavy and rests on dense hardpan, similar to that of the Redding.

Tule gravelly clay loam, collected by R. E. Storie, 2½ miles southwest of Springville, Tulare County, California—No. 18890 (0-15 inches), No. 18891 (15-19 inches).

The *Maxwell* soils are black adobe clays derived from serpentine rocks. They are usually recently deposited heavy clay and may be several feet deep but show only slight evidence of segregation within the profile. There are many comparatively small areas of these soils in California. The Maxwell series is characterized by extreme infertility. The area of Maxwell adobe clay sampled has been repeatedly seeded to barley, but crop failure has always resulted. The native vegetation is predominantly anise; near-by soils of other types were originally covered with various natural grasses.

Maxwell adobe clay, collected by C. F. Shaw and W. P. Kelley from Wooden Valley, Napa County, California—No. 17399 (0-18 inches).

CHEMICAL ANALYSIS

The results of fusion analysis of the colloids are given in a series of tables. Since the colloids were Ca-saturated, the amounts of Mg, K, and Na found represent nonreplaceable forms of these elements. In some of the samples a small percentage of the Ca was also nonreplaceable, although the greater part was replaceable.

Table 1 shows the composition of the Yolo soil colloids. It will be noted that the Yolo silt loam colloid from Davis, California, is remarkably uniform in composition from the surface of the soil down to a depth of 48 inches. The MgO content is comparatively high, and K₂O and Na₂O are low. As has been mentioned, these bases were present in the samples in nonreplaceable forms, whereas the greater part of the CaO was replaceable. The content of SiO₂, Al₂O₃, and Fe₂O₃ was approximately the same in each of the samples from Davis. Apparently, the same kind of colloidal material occurs throughout this profile. The Yolo adobe clay colloid from Gilroy (No. 7083) contained slightly less SiO₂ and more Fe₂O₃ and K₂O than the Davis colloids. Otherwise, they are similar in composition. On the other hand, colloid 431 from La Habra contains considerably less MgO, Al₂O₃, and Fe₂O₃, and relatively more SiO₂ than the other Yolo clay colloids. As will be shown later, the optical properties of this colloid differ somewhat from those of the Davis and Gilroy samples.

Although the authors of this paper do not attach great significance to the molecular ratios of materials of this sort, the data assembled in table 2 show that the SiO₂-Al₂O₃ and SiO₂-R₂O₃ ratios are relatively high in the Yolo clay colloids. No significant differences in these ratios were found in the colloids from the different horizons of the Davis Yolo silt loam, the SiO₂-Al₂O₃ ratio being approximately 4 and the SiO₂-R₂O₃ ratio about 3. The Gilroy sample gave somewhat lower molecular ratios and the La Habra sample definitely higher ratios than the Davis colloids. The base-exchange capacity of the Yolo clay colloids, as determined by the ammonium acetate method, was

comparatively high. The fact that the content of replaceable Ca agrees closely with the NH_4 absorbed from ammonium acetate, both in this and all other series reported in this paper, indicates that the samples were truly Ca-saturated.

Chemical analysis of the Vina samples (table 3) shows certain striking differences which distinguish these colloids from the Yolo clay colloids reported

TABLE 1
Chemical analysis of Ca-saturated Yolo colloids

SAMPLE NUMBER	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	P_2O_5	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O	TOTAL
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
431	48.34	16.92	9.25	0.83	0.04	0.27	2.13	2.99	1.97	0.66	18.20	101.60
7083	40.53	18.65	12.30	1.05	0.05	0.28	2.64	4.26	1.57	0.52	18.00	99.85
17557	43.92	18.65	10.22	0.24	0.11	0.32	1.72	4.59	0.47	0.45	19.00	99.69
17558	43.84	18.13	10.94	0.27	0.11	0.32	1.73	4.72	0.48	0.46	19.30	100.30
17559	44.71	18.25	10.72	0.38	0.08	0.26	1.80	4.85	0.52	0.46	19.00	101.03

TABLE 2
Molecular ratios and base-exchange capacity of Yolo colloids

SAMPLE NUMBER	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	BASE-EXCHANGE CAPACITY		pH OF ORIGINAL SOIL
			Replaceable Ca	Absorbed NH_4	
			m.e.	m.e.	
431	4.85	3.60	67.6	68.1	6.90
7083	3.69	2.61	66.9	67.0	6.98
17557	4.00	2.97	56.5	56.2	7.10
17558	4.12	2.98	57.7	58.5	7.11
17559	4.16	3.03	56.4	56.9	7.10

TABLE 3
Chemical analysis of Ca-saturated Vina colloids

SAMPLE NUMBER	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	P_2O_5	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O	TOTAL
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
16054	40.59	22.84	10.95	0.80	0.04	0.46	2.10	0.55	1.05	0.14	20.35	99.87
16055	40.11	23.15	11.48	0.79	0.06	0.29	2.10	0.55	0.94	0.23	19.77	99.47
16056	40.02	20.61	10.50	0.56	0.04	1.19	1.65	1.23	0.48	0.41	23.20	99.89

in table 1. These differences are chiefly in the much lower MgO and the higher Al_2O_3 content of the Vina colloids, the latter being reflected, of course, in the ratios of SiO_2 to Al_2O_3 and SiO_2 to R_2O_3 (compare tables 2 and 4). Whereas the SiO_2 - Al_2O_3 ratio is approximately 4 in the Yolo clay colloids, it is more nearly 3 in the Vina colloids. The base-exchange capacities of the Yolo and Vina colloids, however, are not significantly different.

Although both the Keefers and the Vina soils have been derived from basic igneous rocks, the chemical analyses of the colloids show certain differences (compare tables 3 and 5). The Keefers clay colloids contain less SiO_2 and more Al_2O_3 and Fe_2O_3 than the Vina. These differences are reflected in the molecular ratios (compare tables 4 and 6). The base-exchange capacity of the Keefers clay colloids is only slightly more than half that of the Vina.

The Sierra clay colloids were found to contain substantially more Al_2O_3 and correspondingly less Fe_2O_3 than the Keefers (compare tables 5 and 7).

TABLE 4
Molecular ratios and base-exchange capacity of Vina colloids

SAMPLE NUMBER	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	BASE-EXCHANGE CAPACITY		pH OF ORIGINAL SOIL
			Replaceable Ca	Absorbed NH_4	
			<i>m.e.</i>	<i>m.e.</i>	
16054	3.02	2.25	64.2	61.7	6.68
16055	2.94	2.24	65.0	64.0	6.65
16056	3.30	2.49	58.0	60.0	6.62

TABLE 5
Chemical analysis of Ca-saturated Keefers colloids

SAMPLE NUMBER	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	P_2O_5	CaO	MgO	K_2O	Na_2O	H_2O	TOTAL
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
16057	36.43	25.97	13.76	1.12	0.09	0.92	0.95	0.65	1.08	0.35	18.98	100.30
16058	36.14	26.28	13.68	1.28	0.20	1.08	1.00	0.65	0.77	0.56	17.95	99.59

TABLE 6
Molecular ratios and base-exchange capacity of Keefers colloids

SAMPLE NUMBER	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	BASE-EXCHANGE CAPACITY		pH OF ORIGINAL SOIL
			Replaceable Ca	Absorbed NH_4	
			<i>m.e.</i>	<i>m.e.</i>	
16057	2.38	1.78	34.7	35.1	6.69
16058	2.34	1.76	34.6	35.5	6.66

The composition was similar throughout the depth sampled. The content of SiO_2 and MgO was somewhat higher in the Sierra than in the Keefers. The SiO_2 - Al_2O_3 ratios were approximately 2 and the SiO_2 - R_2O_3 ratios about 1.70 (table 8). The base-exchange capacity was low, being approximately one-half that of the Keefers colloids.

Tables 9 and 10 show that the composition of the different samples of Redding clay colloids varies considerably. The SiO_2 - Al_2O_3 ratio varied from 2.02 to 3.47, and the SiO_2 - R_2O_3 ratio from 1.71 to 2.65. The base-exchange capacities were found to be roughly proportional to the SiO_2 - Al_2O_3 ratios.

The Olinda Redding clay colloids are not significantly different in mass composition from the Sierra colloids. All the other Redding samples contain

TABLE 7
Chemical analysis of Ca-saturated Sierra colloids

SAMPLE NUMBER	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	P ₂ O ₅	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O	TOTAL
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
16308	38.68	31.47	10.04	0.66	0.14	0.42	0.61	1.96	0.86	0.46	13.95	99.25
16309	38.93	32.69	9.72	0.76	0.08	0.27	0.49	1.52	0.84	0.36	13.30	98.96
16310	39.12	33.58	9.08	0.60	0.04	0.29	0.45	1.05	0.52	0.33	15.30	100.36
16311	39.78	32.93	9.20	0.75	0.04	0.34	0.45	1.16	0.18	0.27	15.10	100.20

TABLE 8
Molecular ratios and base-exchange capacity of Sierra colloids

SAMPLE NUMBER	SiO ₂ / Al ₂ O ₃	SiO ₂ / R ₂ O ₃	BASE-EXCHANGE CAPACITY		pH OF ORIGINAL SOIL
			Replaceable Ca	Absorbed NH ₄	
			m.e.	m.e.	
16308	2.09	1.75	21.9	22.7	5.81
16309	2.03	1.70	18.8	19.6	5.48
16310	1.98	1.69	16.2	16.0	6.00
16311	2.06	1.74	16.0	16.4	6.65

TABLE 9
Chemical analysis of Ca-saturated Redding soil colloids

SAMPLE NUMBER	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	P ₂ O ₅	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O	TOTAL
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
16303	43.27	30.69	8.12	0.45	0.01	0.36	0.55	1.09	0.23	0.22	15.10	100.09
16304	44.56	29.19	8.40	0.51	0.1	0.35	0.82	0.78	0.29	Tr.	16.20	101.10
16305	42.93	28.57	10.55	1.08	0.02	0.36	0.63	0.87	0.82	0.67	13.29	99.79
16306	42.77	29.50	7.85	0.86	Tr.	0.36	0.67	0.80	0.45	0.32	16.16	99.74
16307	43.36	30.23	6.96	0.68	Tr.	0.37	0.90	0.77	0.40	0.39	15.52	99.58
16314	42.80	26.89	9.75	0.48	0.90	0.42	1.10	1.12	0.11	0.21	17.20	100.08
16315	43.72	22.38	9.67	0.45	0.10	0.29	1.70	1.93	0.13	0.16	18.90	99.43
16316	43.52	21.35	10.20	0.40	0.01	0.25	1.55	1.66	0.16	0.24	20.10	99.44
16317	40.47	29.15	8.52	0.57	0.17	0.40	0.90	1.27	0.19	0.25	17.90	99.79
16318	40.87	27.64	9.96	0.45	0.07	0.48	0.99	1.16	0.15	0.19	17.80	99.76
16319	39.68	32.52	8.76	0.30	0.06	0.45	0.56	1.18	0.12	0.19	16.40	100.22
16320	39.40	32.94	9.10	0.39	0.02	0.42	0.50	0.89	0.13	0.23	16.00	100.02
16321	39.24	32.98	8.57	0.45	0.02	0.44	0.57	0.89	0.16	0.23	16.30	99.85

somewhat more SiO₂ and less Al₂O₃ than the Sierra. It will be noted that the colloid of the Redding profile at Palermo differs markedly in composition from the Redding samples of other localities. As will be brought out in later

sections of this paper, the optical and x-ray investigations also showed that this profile is different from the other Redding soils.

The Redding clay colloid from Oroville profile is remarkably similar to that of the Kearney Mesa. This is surprising because of the difference in the annual rainfall of these areas, namely, 20 to 30 inches at Oroville and only 10 to 12 inches on the Kearney Mesa. It is also interesting to note that the

TABLE 10
Molecular ratios and base-exchange capacity of Redding colloids

SAMPLE NUMBER	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	BASE-EXCHANGE CAPACITY		pH OF ORIGINAL SOIL
			Replaceable Ca	Absorbed NH_4	
			<i>m.e.</i>	<i>m.e.</i>	
16303	2.39	2.04	21.2	23.2	5.51
16304	2.59	2.19	30.5	34.6	4.92
16305	2.55	2.07	23.1	22.9	5.40
16306	2.47	2.11	23.5	23.9	5.00
16307	2.44	2.13	31.9	32.0	4.82
16314	2.67	2.20	38.9	39.4	6.70
16315	3.32	2.60	60.2	59.2	5.75
16316	3.47	2.65	55.4	55.5	5.75
16317	2.36	1.99	31.9	30.9	5.50
16318	2.51	2.04	35.4	35.5	5.35
16319	2.07	1.77	19.9	19.7	5.62
16320	2.03	1.73	18.7	18.2	5.28
16321	2.02	1.71	19.2	18.5	5.05

TABLE 11
Chemical analysis of Ca-saturated San Joaquin colloids

SAMPLE NUMBER	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	P_2O_5	CaO	MgO	K_2O	Na_2O	H_2O	TOTAL
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
18882	46.51	23.92	9.76	1.00	0.18	0.26	1.17	1.54	1.61	0.40	14.20	100.55
18883	46.49	23.18	10.37	1.10	0.13	0.26	1.30	1.46	1.26	0.34	14.26	100.15
18884	48.04	20.41	10.35	1.30	0.16	0.19	1.23	2.11	1.44	0.46	14.06	99.75
18885	48.31	21.59	10.40	1.10	0.13	0.16	1.18	3.02	1.56	0.46	13.00	100.91
18888	44.96	23.35	10.69	1.20	0.24	0.18	1.27	2.73	1.84	0.19	14.23	100.88
18889	45.75	25.70	8.96	1.30	0.17	0.18	1.11	2.72	1.50	0.30	14.35	102.04
6530	44.62	23.74	9.92	0.54	0.05	0.51	0.76	2.33	1.43	Tr.	15.96	99.86

colloid of the A horizon of the Kearney Mesa samples has lower base-exchange capacity than that of the B horizon. The same is true of the Oroville and Palermo samples, but it is not true of those from Olinda.

Analysis shows that the San Joaquin soil colloids from the different profiles (table 11) are remarkably similar in elementary composition and that the A and B horizons are also similar in composition. The samples from the Pixley area, Terra Bella, and Lindcove contain more calcium than that from

Fairmead. It is interesting to note that the $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-R}_2\text{O}_3$ ratios are comparatively high (see table 12). The base-exchange capacity was approximately the same in all the samples except that from Fairmead, which was comparatively low, despite the fact that its molecular ratios are relatively high. This shows that there is no certain relationship between base-exchange capacity and the ratio of SiO_2 to Al_2O_3 or SiO_2 to R_2O_3 .

TABLE 12
Molecular ratios and base-exchange capacity of San Joaquin colloids

SAMPLE NUMBER	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	BASE-EXCHANGE CAPACITY		pH OF ORIGINAL SOIL
			Replaceable Ca	Absorbed NH_4	
			m.e.	m.e.	
18882	3.31	2.63	43.1	43.9	7.21
18883	3.41	2.65	47.2	48.0	8.26
18884	4.00	3.03	43.6	44.0	6.91
18885	3.81	2.92	43.7	44.3	8.11
18888	3.27	2.53	40.0	40.5	7.41
18889	3.02	2.47	39.5	40.0	7.21
6530	3.20	2.53	27.0	27.6	7.17

TABLE 13
Chemical analysis of Ca-saturated Hanford colloids

SAMPLE NUMBER	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	P_2O_5	CaO	MgO	K_2O	Na_2O	H_2O	TOTAL
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
7095	42.41	20.33	13.12	0.30	0.09	0.38	1.94	3.00	0.60	Tr.	17.81	99.98
18886	47.22	23.63	10.84	0.40	0.13	0.26	1.59	3.32	1.77	0.46	14.04	103.66
18887	44.35	21.83	11.34	0.80	0.17	0.24	1.51	3.15	2.02	0.34	14.11	99.86

TABLE 14
Molecular ratios and base-exchange capacity of Hanford colloids

SAMPLE NUMBER	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	BASE-EXCHANGE CAPACITY		pH OF ORIGINAL SOIL
			Replaceable Ca	Absorbed NH_4	
			m.e.	m.e.	
7095	3.55	2.51	47.4	47.9	7.70
18886	3.41	2.63	57.5	56.0	7.83
18887	3.45	2.59	45.7	46.5	8.11

Chemical analyses of the Hanford clay colloids (table 13) gave results similar to those of the San Joaquin colloids reported in table 11. This similarity is further shown by their molecular ratios and base-exchange capacities (compare tables 12 and 14). The $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio of the Hanford colloids was approximately 3.50, the $\text{SiO}_2\text{-R}_2\text{O}_3$ ratio about 2.60, and the base-exchange capacity approximately 50 m.e. per 100 gm.

Since only a single sample each of the Ramona, Placentia, Tujunga, Madera, and Maxwell soils was investigated it is not necessary to discuss the results in detail. It will be noted, however, that the Tujunga, which is classified as the youngest member of the San Joaquin family of soils, contains colloid of composition similar to that of the San Joaquin series, which is the oldest member of this family (compare tables 11 and 15). On the other hand, the Ramona and Placentia soils are classified as intermediate members of the San Joaquin family, but the chemical analysis of the colloids of these two samples differs considerably from that of both the Tujunga and the San Joaquin soils. The

TABLE 15
Chemical analysis of Ca-saturated colloids from soils of various series

SAMPLE NUMBER	SERIES	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	P ₂ O ₅	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O	TOTAL
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
7091	Ramona	41.12	27.51	10.88	0.89	2.54	0.80	Tr.	15.42	99.16
7092	Placentia	39.62	29.85	8.60	0.35	0.02	0.34	0.69	2.73	0.76	Tr.	15.98	98.94
7094	Tujunga	43.75	21.20	9.92	0.45	0.08	2.21	2.58	0.60	0.20	18.40	99.39
6528	Madera	41.96	23.35	10.60	0.38	0.06	0.41	1.36	3.17	0.50	Tr.	17.62	99.41
18890	Tule	43.60	19.20	13.02	1.00	0.12	0.16	1.46	1.97	1.26	0.19	16.36	98.34
18891	Tule	43.43	24.00	9.44	1.20	0.04	0.21	1.72	1.95	0.30	0.19	18.07	100.55
17399	Maxwell	44.08	15.85	9.20	0.16	0.04	0.11	1.82	10.25	0.17	0.16	17.80	99.64

TABLE 16
Molecular ratios and base-exchange capacity of various soil colloids

SAMPLE NUMBER	SERIES	SiO ₂ Al ₂ O ₃	SiO ₂ R ₂ O ₃	BASE-EXCHANGE CAPACITY		pH OF ORIGINAL SOIL
				Replaceable Ca	Absorbed NH ₄	
				m.e.	m.e.	
7091	Ramona	2.54	2.03	27.8	27.7	7.13
7092	Placentia	2.26	1.91	24.7	24.8	7.11
7094	Tujunga	3.50	2.70	56.5	57.2	7.57
6528	Madera	3.04	2.36	45.7	46.1
18890	Tule	3.86	2.70	42.0	43.4	7.58
18891	Tule	3.03	2.45	55.1	56.4	7.07
17399	Maxwell	4.74	3.45	63.0	65.1	6.94

Madera clay colloid is similar to that of the San Joaquin both in elementary composition and in base-exchange capacity (compare tables 12 and 16). Before definite conclusions can be drawn concerning the relations between composition and properties of colloid and maturity of profile, it will be necessary to investigate a considerable number of profiles of these and other soil series. The data presented herein, although not conclusive, do not indicate any significant relation between quality of colloids and maturity of profile.

Analyses of the colloid from the Tule soil profile show that it is similar to the San Joaquin colloid in composition and base-exchange property.

The Maxwell adobe clay colloid is strikingly different from any other soil colloid reported in this paper. The content of Al_2O_3 is low and the MgO very high. The base-exchange capacity of this sample was relatively high, being approximately the same as that of the Yolo, Vina, and the Palermo samples of the Redding. The $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-R}_2\text{O}_3$ ratios are high, because of the low content of Al_2O_3 . The composition of this colloid is similar to that of serpentine soils from other localities in the United States, as reported by Robinson, Edgington, and Byers (32).

DEHYDRATION INVESTIGATIONS

Samples of the colloids were first brought to comparable moisture conditions by exposing them to an atmosphere of known moisture content until their weights were constant. The water vapor pressure used was that of a 52 per cent solution of sulfuric acid at a temperature of 25°C ., which roughly corresponds to the average minimum atmospheric moisture at Riverside, California, where this investigation was made. The dehydrations were made against an atmosphere of approximately constant moisture content, provided by passing a current of air first through 52 per cent sulfuric acid (by volume), then through the electric furnace in which the samples were heated. The samples were held in the furnace at each temperature until constant in weight. The results are shown by a series of graphs, only typical representatives of the different types of the curves being shown. Except as indicated below, the several horizons of each soil type gave almost identical dehydration curves.

The dehydration curves of the different Yolo clay colloids have a similar wavelike shape (fig. 1). Those for the Davis samples resemble the curves for montmorillonite and beidellite [see Kelley, Jenney, and Brown (24)]. Attention is directed to the relatively large water loss at 100° and 150°C .

The curves for the Vina and the Keefers clay colloids (fig. 2) are approximately parallel and show deflections between 300° and 400°C . These colloids seem to resemble finely ground kaolinite and halloysite. As will be shown later, all the colloids reported in this paper are definitely crystalline. Either the crystals of the Vina and Keefers samples are extremely small, however, or else they contained considerable amorphous material. Special attention is drawn to that fact that at the lower temperatures the water losses of Vina colloid 16055 were similar to those of the Yolo samples, whereas those of the Keefers sample 16058 were substantially less. In each case the loss was roughly proportional to the base-exchange capacity.

The Sierra and most of the Redding clay colloids (fig. 3) gave remarkably similar dehydration curves, which closely approach that of the Cecil clay colloid from the Piedmont Plateau, as reported by Kelley and his co-workers (24, 25). Pronounced deflections in the curves were noted between 300° and 400°C . These curves strongly suggest halloysite or kaolinite (34, 35). The Kearney Mesa samples from the Redding soils and certain of the samples from northern California proved to be almost identical. On the other hand,

the curves for the B and C horizons of the Redding at Palermo (fig. 4), although of the same general shape, nevertheless show that these colloids contain considerably more low-temperature water. The evidence is that these samples contain considerably greater percentages of nonkaolinitic clay minerals than do the other Redding samples. The colloid of the A horizon of the Palermo Redding soil differs from that of the B horizon in that the low-temperature water of the latter was the greater. Otherwise their dehydration curves were similar.

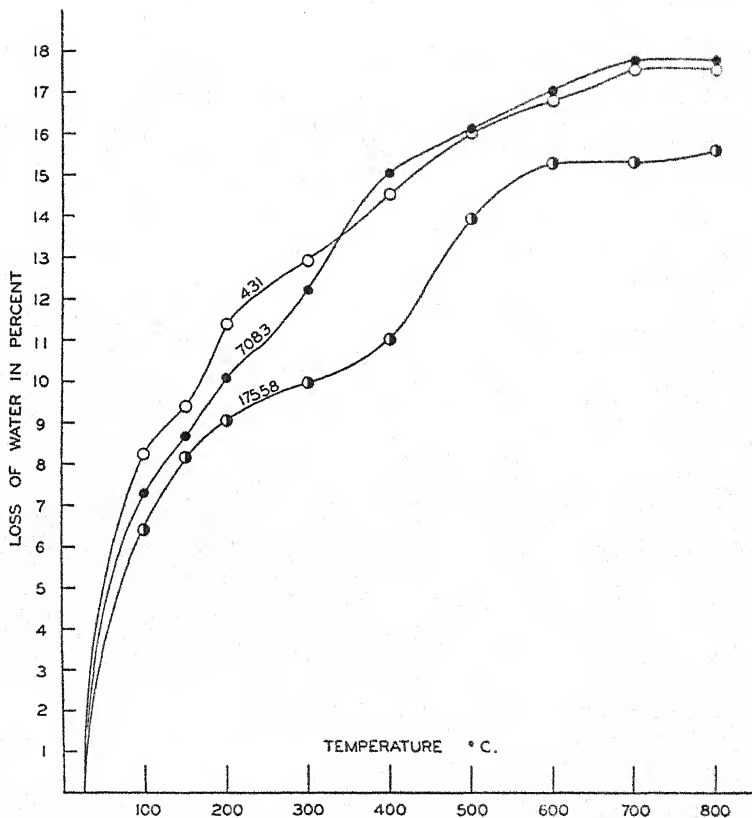


FIG. 1. DEHYDRATION CURVES OF YOLO COLLOIDS, 431, 7083, AND 17558

Although certain features of the Tule soil are suggestive of the San Joaquin series, the dehydration curves were remarkably like those of the Redding Palermo clay colloids.

The San Joaquin and Hanford clay colloids (fig. 5) gave dehydration curves of approximately the same shape, both showing pronounced deflections. These curves differ from those of the Sierra and Redding chiefly in that the deflections occur at higher temperatures. This indicates a different type of

clay mineral. As will be shown later, the Sierra and most of the Redding samples are definitely kaolinitic, whereas the San Joaquin and Hanford clay colloids resemble illite (13).

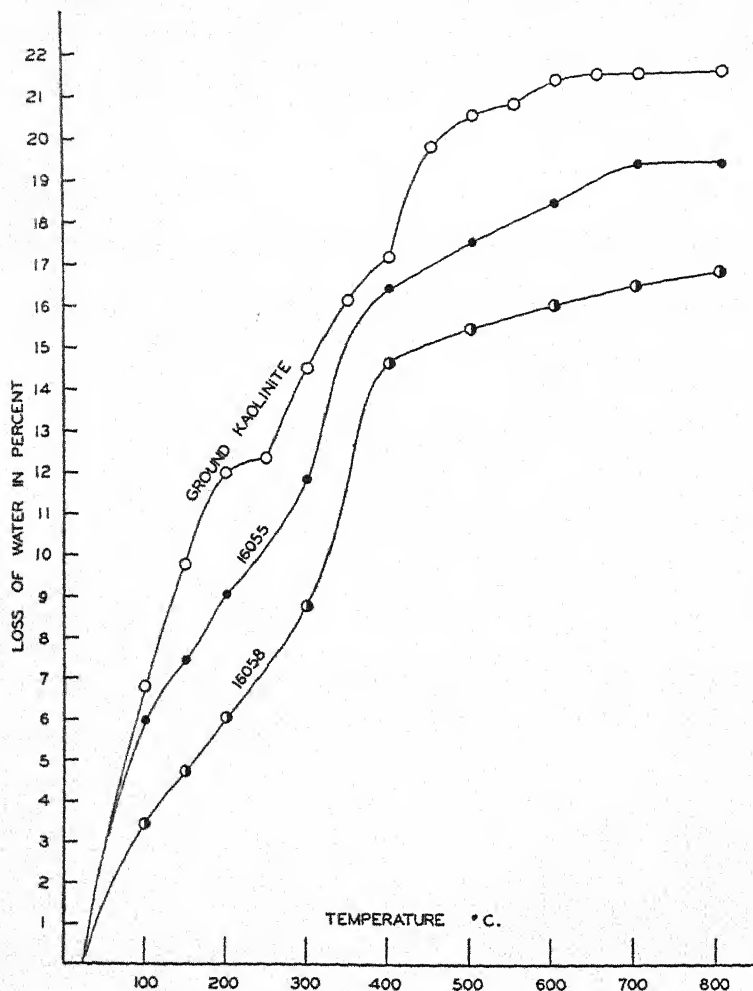


FIG. 2. DEHYDRATION CURVES OF VINA (16055) AND KEEFERS (16058) COLLOIDS AND OF FINELY GROUND KAOLINITE

RESULTS OF MICROSCOPICAL STUDY

The colloid samples discussed in the foregoing sections of this paper were studied in oil and water mounts with a Leitz CM petrographical microscope, using artificial light and a daylight filter. The series of oils used had indexes spaced at intervals of approximately .005, and were checked two or three times by means of a Spencer Abbe refractometer. The refractometer was

tested with standard glass plates of both high and low indexes and was found to have an accuracy beyond our needs.

In consequence of evaporation and the other treatments, the minute particles of the original colloidal suspension in almost all the samples had gathered into relatively large optical units commonly 0.1 mm. and rarely 1 mm. in diameter. These units were recognized by their double refraction. Hendricks and Fry (17) have briefly described the same effect, and Grim (12) has discussed it more fully. The indexes of refraction of these compound par-

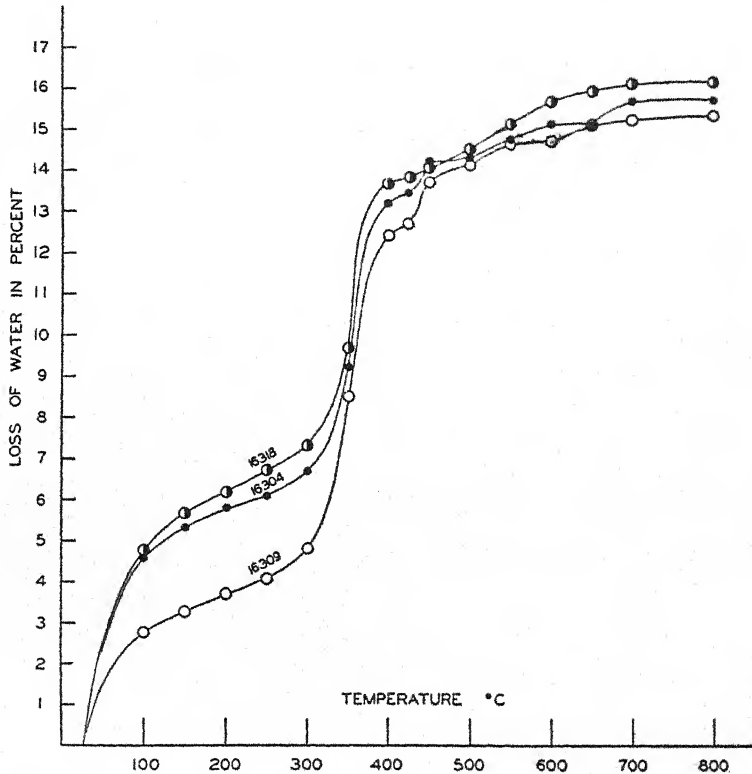


FIG. 3. DEHYDRATION CURVES OF REDDING COLLOIDS (16304 FROM SOUTHERN CALIFORNIA AND 16318 FROM NORTHERN CALIFORNIA) AND SIERRA COLLOID 16309

ticles were determined by the method of central illumination (26), the usual corrections for temperature being made.

The clay aggregates have a smooth jellylike appearance under the microscope, but virtually all of them were more or less platy or flaky. Wherever determinable, the optical character was found to be negative, with the acute bisectrix perpendicular to the plates or within 30° of that position. The poor interference figures given by the samples were uniaxial or biaxial with small optic angles (2V).

Rigorous study of the probable error of the index determinations was not made. Almost all the determinations, however, were repeated once, and some of them many times. Concurrent studies on bentonite also gave information concerning the range of experimental error. The maximum variations for single samples found in the earlier part of this study were as follows: soil clay aggregates, alpha .013, beta .012, gamma .010; Ca-saturated bentonite

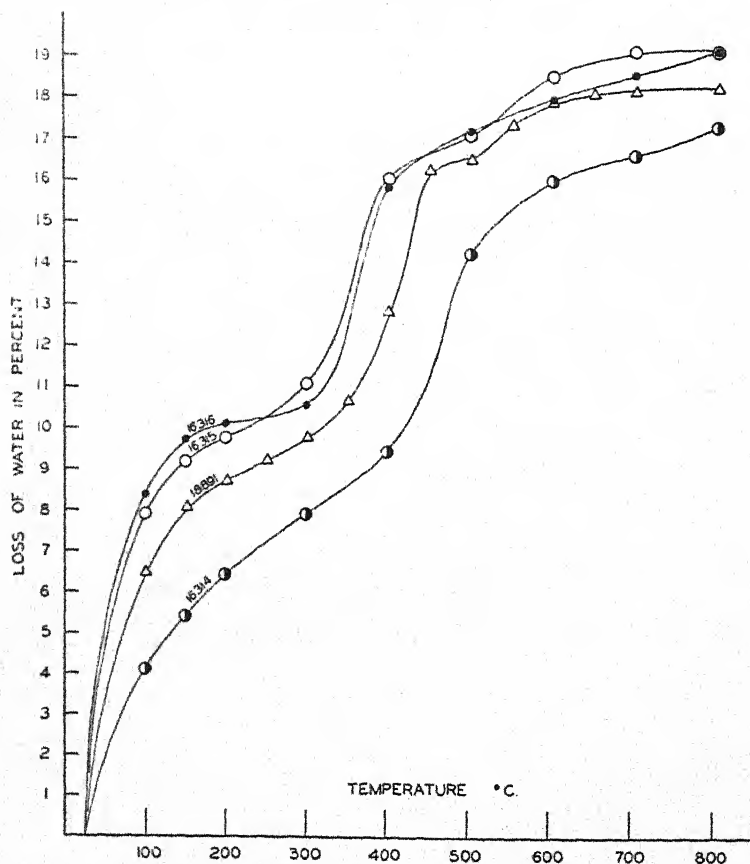


FIG. 4. DEHYDRATION CURVES OF REDDING COLLOIDS FROM PALERMO, 16314 (3-18 INCHES), 16315 (20-40 INCHES), AND 16316 (47-64 INCHES), AND OF TULE COLLOID 18891 (15-19 INCHES)

colloids, alpha .030, beta .022, gamma .026. Variations in moisture content were at once suspected of being involved; consequently, a sample of bentonite from Otay, California, one of the most variable bentonites, was exposed over water in a desiccator for 56 hours and also over concentrated H_2SO_4 . Gamma over water was found to be 1.470 and over H_2SO_4 1.520.

The earlier optical study was carried out in Riverside during the summer of

1932 when the relative humidity at 8:30 a.m. ranged from 26 to 94, and averaged 69. Later work, from September, 1932, to September, 1934, was on samples exposed in 1- to 2-mm. films over 52 per cent H_2SO_4 , giving a humidity of approximately 30. Every sample was determined at least once over 52 per cent H_2SO_4 , at room temperatures ranging from 20° to 25°C .

The indexes for Ca-saturated clay aggregates, as given in table 17, are thought to be accurate in most cases to $\pm .003$. The colloids with high indexes and low double refraction gave less satisfactory results, accurate to perhaps

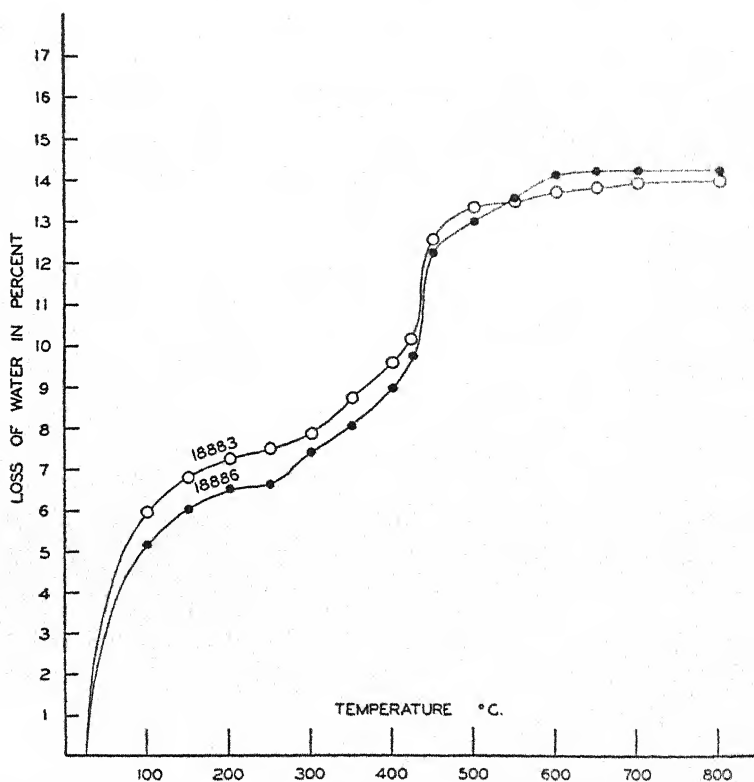


FIG. 5. DEHYDRATION CURVES OF SAN JOAQUIN COLLOID 18883 AND HANFORD COLLOID 18886

$\pm .005$. Since the Keefers samples 16057 and 16058 showed poorly formed flakes or deep color or both, the determinations in these cases are still more doubtful, with an accuracy of perhaps $\pm .010$. The various errors are thought to be due (a) to residual moisture differences caused by variations in temperature and hence of water vapor pressure and also to incomplete equilibrium with the atmosphere of the desiccator in the lower parts of the samples, thin though they were, and (b) to innate difficulties in the index determinations, due largely to the abundant inclusions mentioned below. The determination of alpha is most difficult because the flakes must be on edge.

TABLE 17
Optical properties of Co-saturated clay aggregates from soils

SERIES	LABO- RATORY NUMBER	DR* per cent	INDEXES OF REFRACTION			$\gamma - \alpha$	2V†	EXTINCTION	NOTES
			Alpha	Beta	Gamma				
Tujunga Hanford Ramona Placentia San Joaquin Madera	7094	100	1.553	1.569	1.569	0.016		0-35°	Irregular plates
	7095	100	1.567	1.580	1.580	0.013		0°	Indexes variable
	7091	100	1.581	1.591	1.591	0.010		0° approx.	Indexes variable
	7092	100	1.574	1.587	1.587	0.013		0-20°, 38°	Fair plates
	6530	100	1.563	1.576	1.579	0.016		0°	Rather poor plates
	6528	100	1.551	1.569	1.569	0.018	Near 0°	0-30°	Good plates and ext.
Vina	16054	33	1.568		1.573	0.005		0° usually	67% isotropic, n 1.570
	16055	100—	1.564	1.572	1.572	0.008		0° usually	Rarely (—) elong.
	16056a	100?	1.571		1.574	0.003		0° usually	Rarely (—) elong.
	16056b	100	1.564	1.582	1.583	0.019		0° usually	Much rarer than 16056a
Keefers	16057	Little	n = 1.60+; no large grains						
	16058	Little	n = 1.610 ± 0.010; no large birefringent grains except mica (?) shreds						
Yolo A A B C A	7083	100	1.567	1.586	1.587	0.020		0-15°	Rarely lower indexes
	17557	100	1.551	1.572	1.574	0.023		0° usually	
	17558	100	1.556	1.574	1.576	0.020		0° usually	Very good plates
	17559	100	1.555	1.573	1.574	0.019		0°	
	431	100	1.554	1.569	1.569	0.015		0° usually	Indexes vary; rare (—) elong.; impure

Redding A	16303	100	1.584	1.593	1.594	0.010	Near 0°	0° up 0°-30°	Good plates Good plates; "rare (-) elong." Much rarer than 16304a Also lower indexes Like 16305 Like 16304
B	16304a	100-	1.569	1.579	1.580	0.011			
B	16304b	100	1.557±		1.573±	0.016		0-40°	
A	16305	100-	1.593		1.600	0.007		0°	
B ₁	16306	100-	1.584	1.594	1.594	0.010		0-28°	
B ₂	16307	100	1.557	1.569	1.569	0.012			
Redding A	16314	100-	1.575	1.583	1.583	0.008		0°	Poor flakes
B ₁	16315	100	1.535	1.548	1.550	0.015		0-40°	Good plates; also some with higher indexes, $\gamma = 1.558$
B ₂	16316	100	1.533	1.550	1.553	0.020		0-30°	Indexes vary
A	16317	100?	1.598		1.601	0.003		0°-30°	Poor flakes; tests vague
B	16318	100	1.588		1.596	0.008		0-40°	Poor flakes; indexes vary
A	16319	100?	1.601+		1.604+	0.003			Poor flakes
B ₁	16320	100?	1.598	1.604	1.604	0.006		0°?	Fair flakes
B ₂	16321	100	1.592	1.598?	1.600	0.008		0°?	Fair flakes
Sierra	16308	100	1.590	1.597	1.600	0.010		0-30°	Micaceous inclusions
	16309	100-	1.592		1.604	0.012		0-30°	Micaceous inclusions
	16310	100	1.590	1.602	1.604	0.014		0-10°	Micaceous inclusions
	16311	100	1.592		1.603	0.011		0-15°	Micaceous inclusions
Maxwell	17399	100	1.544	1.560	1.560	0.016	0°+	0-20°	Indexes vary; γ 1.556-1.562

* DR = Double refraction.

† 2V given only for the rare cases in which fairly good interference figures were observed.

Double refraction was calculated from the indexes, but not entirely without check. In determining the indexes, the double refraction indicated by the interference colors was kept in mind. In a few cases it was possible to calculate the double refraction from the width of a flake and its interference tint when on edge. For example, Redding colloid 16303 was found to have $\gamma - \alpha = 0.010$ both by the difference between the measured indexes and by calculation from the interference tint. For the major part of Redding 16304 the indexes indicated $\gamma - \alpha = 0.011$, and a flake on edge gave an interference tint corresponding to $\gamma - \alpha = 0.009$.

In general the double refraction as given, even where a nearly pure clay mineral is concerned, may be too low, because of optical compensation in the compound flakes, or too high, because of the addition of form double refraction to the proper double refraction of the clay mineral.

The flaky aggregates of the different clays ranged from pale yellow-brown to very dark brown in color. No pleochroism was certainly observed. In general, the darker is the color, the higher are the indexes and the lower is the double refraction, but this is only a very rough correlation.

Extinction was commonly somewhat vague and undulatory, but in some of the paler, more definitely platy clays it was perfectly sharp. Where the extinction was most definite, the double refraction was found to be highest, and this suggests that the differences in double refraction given in table 17 are exaggerated, the lower values being in part due to compensation between differently oriented portions of a given flake. The fact that more or less complete extinction can be obtained, however, indicates that in such cases the various parts of a single flake occur in approximately similar orientation, especially with respect to the X optical direction (alpha index).

The large, birefringent optical units thus far discussed are crowded with innumerable minute inclusions. These are usually irregularly equidimensional, but inclusions were found in the shape of definite rods and flakes from 3 to 15 μ in diameter or length. Some of the apparent inclusions may have been mere cavities, analogous to the systems of tubes and bubblelike spots such as have been observed in the mineral anauxite from Ione clay of California. But the evidence indicates that the minute inclusions in the soil clays were chiefly solid. Many of them were birefringent. Furthermore, the inclusions stand out from the host grains in high relief, indicating that they are of different index and density and presumably of different composition.

Some of the minute inclusions have been identified by the use of an oil immersion objective and 20 x ocular. Limonite or similar iron oxide is abundant, and rutile, zircon (?), quartz, muscovite, bleached biotite (?), and other minerals were also present. Color and relief suggest that a large part of the inclusions may have been iron oxide. The minute inclusions were relatively scarce in the Sierra clay colloids, and at least half of those present were birefringent. The greater part of the birefringent inclusions are yellow flakes, thought to be weathered mica.

The Keefers samples were unique among those studied, in that they yielded no large birefringent units. The samples were composed entirely of minute grains, most of which showed no birefringence even under the oil immersion objective. Birefringent rods and needles of rutile up to $15\ \mu$ in length were recognized in these samples, and other minute prisms of paler color were seen which may have been zircon or possibly some other mineral. The isotropic portion of the samples included brown grains of high index which are considered to be limonite, and by far the greater part of the Keefers samples consists of minute, brownish, angular, isotropic grains which individually showed high relief in the media used, but which in aggregates seemed to have the indexes listed in table 17.

Study of natural colloids. For comparison with the Ca-saturated form of these colloids, a few samples of untreated aqueous suspensions, obtained directly from the original soils, were dried below 100°C . and studied in oils. These and the Ca-saturated materials yielded almost identical results. For example, the Yolo clay 7083, the one most thoroughly investigated in the untreated state, gave values of gamma ranging from 1.583 to 1.588 as compared with 1.587 for the Ca-saturated form. Other optical properties of this colloid, likewise, were found to be similar, except that alpha seemed to be slightly higher in the untreated form and the birefringence correspondingly lower. It is concluded that the values given in table 17 for the Ca-saturated materials may be taken as characteristic of the natural substances.

Effects of saturation with various bases. Any single soil colloid may show considerable variation in its indexes of refraction, perhaps partly depending upon the base with which it has been saturated. Our results illustrating this point are given in table 18. The variations are not systematic.

Notable differences in the behavior of the Ca- and Na-saturated soil colloids were observed under the microscope, though the differences were of degree rather than of kind. When mounted in oils, both were seen to be made up of relatively large, coherent grains. But in water mount, the flakes of the Ca-saturated form of Yolo 431, for instance, immediately and suddenly suffered partial disintegration to a mixture of doubly refracting grains 40 to $80\ \mu$ in diameter and interstitial minute grains showing Brownian movement. The Na-saturated form of this colloid underwent the same kind of disintegration in water, but much more completely, so that only a few medium-sized flakes remained, with vague boundaries, low birefringence, and hazy extinction, all the rest of the clay fragments having broken down into minute grains showing Brownian movement.

Effect of dispersion. The Na-saturated soil colloid 431 was leached with water, and while still moist was mounted in water for study under the microscope. Only minute grains were to be seen, and when the preparation was made sufficiently dilute, these grains showed Brownian movement. The movement was stopped by the introduction of a little saturated NaCl solution. The progress of the effect was watched as it crossed the microscope slide.

Grains on one side of the field were still dancing, after those on the other side had become quiescent. Then flow of the NaCl solution across the slide caused the grains to collect in small clusters, in which, however, the grains were still perfectly distinct. The individual particles, where shape could be distinguished, did not appear noticeably platy.

A sample of Ca-saturated colloid 431 was digested for 24 hours with 4 *N* NaCl, dispersed in water until no large grains could be seen under the microscope, flocculated by leaching with methyl alcohol, and dried in the laboratory at ordinary temperatures. The Na-saturated product was pulverized and then

TABLE 18
Optical properties of soil colloids saturated with various bases*

SERIES	LAB-ORATORY NUMBER	BASE	DR†	INDEXES OF REFRACTION			$\gamma - \alpha$	EXTINCTION	NOTES
				Alpha	Beta	Gamma			
Yolo	431	Ca	100	1.554	1.569	1.569	0.015	0-18°	Fair flakes
	431	Mg	100—	1.540	1.552	1.554	0.014	0-30	Poor flakes; also higher indexes
	431	K	100	1.558±		1.568±	0.010+	0	Poor flakes
	431	Na	100	1.558		1.570	0.012	0-20	Poor flakes
	7083	Ca	100	1.567	1.586	1.587	0.020	0 usually	Rarely lower n.
	7083	Mg	100	1.567±	1.586	1.586	0.019±	0 approx.	Good plates
	7083	Na	100	1.562	1.580	1.582	0.020	0	Rarely higher n.
	16305	Ca	100—	1.593		1.600	0.007	0	Also lower n.
	16305	Mg	50±	1.591±		1.598±	0.007		
Redding	16305	Na	50±	1.585+		1.590+	0.005	0 approx.	Up to 1.600
	16308	Ca	100	1.590	1.597	1.600	0.010	0-30	
	16308	Mg	100?	1.592		1.600	0.008		Poor flakes
Sierra	16308	Na	100	1.589		1.595	0.006	0 approx.	Poor flakes

* All determinations on thin films after long standing over 52 per cent H_2SO_4 .

† DR = Double refraction.

studied in oils under the microscope. The large optical units were found to have formed again and to have the same optical properties as before dispersal. This experiment proves that the large flakes can be dispersed and formed again, apparently at will.

Effect of time of subsidence. The time of subsidence of the original Yolo soil 7083 was varied in order to test the effect upon the formation of large optical units. First, the upper 8 cm. of an aqueous suspension of the original soil was drawn off after only 1 hour of subsidence. The dried natural colloid thus obtained was studied in oils and found to be made up of minute bodies up to 10 μ in diameter, some of which were enveloped in birefringent, yellow

jellylike masses 20 to 50 μ across. In a second test the upper 8 cm. of the suspension was drawn off after standing 48 hours. In this case the jellylike masses were larger on the average (20 to 60 μ), better formed, more uniformly birefringent, and much more completely enclosing the numerous inclusions. That is to say, 48 hours of settling somehow promoted the formation of the birefringent, jellylike masses upon evaporation of the suspension. In a third test the original 7083 soil was shaken with water in a cylinder and allowed to stand for about a week. A sample of the upper part of the flocculent layer which had settled in the cylinder was then taken, quickly dried below 100°, and studied in oils. It was found to be made up chiefly of flat flakes of a brown, jellylike substance, full of minute inclusions with high relief. These optical units were 50 to 60 μ in diameter and 10 to 15 μ thick. The flaky character was more noticeable than that in the previous samples.

TABLE 19
Effect of oxalic acid treatment of Ca-saturated clay aggregates

SERIES	LABORATORY NUMBER	GAMMA		$\gamma - \alpha$		COLOR CHANGES AND OTHER NOTES
		Before treatment	After treatment	Before treatment	After treatment	
Vina	16055	1.572	1.562	0.008	0.008	Poor flakes before and after; brown to gray-brown
Keefers	16057	1.60+	1.580	Mostly isotropic		Determinations very difficult
Sierra	16058	1.610	1.573	Isotropic	0.000-0.004	Determinations difficult
	16309	1.604	1.570	0.012	0.014	Rich brown to yellow-brown
Redding	16315*	1.550-1.558	1.559	0.015	0.015	Pale brown to lemon-yellow; good plates before and after
	16319	1.604+	1.573	0.003	0.008	Deep brown to pale brown; poor flakes to good plates
	16321	1.600	1.564	0.008	0.012	Rich brown to pale yellow

* After acid treatment sample 16315 gave a biaxial figure with small 2V; the moisture content of this sample had but little effect on the indexes.

Birefringence of moist colloids. Several soil colloid samples were studied while still somewhat moist. Even in these cases large birefringent units of the order of 0.1 mm. had already formed. Some, but not all, of the birefringent units were, in part, pressure effects, "form double refraction" (2), due to smearing the moist colloid in handling.

Effect of oxalic acid treatment. Seven soil colloids were leached for several days with an aqueous solution of oxalic acid and sodium oxalate. The effect is shown in table 19. It will be noted that, in general, the depth of color and the indexes of refraction were reduced and the birefringence was increased by acid treatment. It is also apparent that those soil colloids with the highest indexes showed the greatest reduction in indexes by acid treatment,

and that after the treatment gamma was not greater than 1.580 or lower than 1.559. In every property, and in almost every case, the colloids were more nearly similar after the acid treatment than before.

RESULTS OF X-RAY STUDY

X-ray diffraction patterns from all the colloid samples described in this paper were obtained by the use of molybdenum radiation rendered virtually monochromatic by filtration through zirconia screens. The powdered materials were packed in thin-walled soft glass tubes having an internal diameter of about 0.6 mm. and were exposed in cylindrical cassettes having a radius of 8 inches, which were especially designed to register lines corresponding to spacing as wide as 20Å.

From measurements of the patterns interplanar spacings corresponding to all clearly recognizable lines were recorded. The results are presented in tables 22 to 37. By comparison with suitable reference data for known substances, it has been possible in most cases to decide definitely which classes of clay minerals are present in the colloids and to draw some limited conclusions regarding other constituents. As has been pointed out by Kelley and Dore (21) in an earlier publication, three types of clay minerals may be recognized singly or in admixture, from their diffraction patterns; namely, the kaolinite-halloysite type, the montmorillonite-beidellite type, and the muscovitelike type (designated as the "x" mineral).

In a recent paper by the authors (25), a series of reference spacings for kaolinite and montmorillonite were tabulated. These spacings are reproduced in table 20, to which are added reference spacings for the identification of the "x" mineral. The theoretical basis for the selection of the kaolinite and montmorillonite reference spacings has been discussed in the former paper and will not be repeated here. The reference spacings for the "x" mineral were derived from the data recently published by Grim, Bray, and Bradley (13).

These investigators have isolated from argillaceous sediments in Illinois, a clay mineral which appears to be similar to, if not identical with, the muscovite-like clay mineral mentioned by Ross and Kerr (35), the mineral designated by Endell, Hofmann, and Maegdefrau (10) as "Glimmerton," and the third type of clay mineral found in California soils. The name "illite" was proposed by them as a group name to designate "the clay mineral constituent of argillaceous sediments belonging to the mica group." Five samples of illite isolated by these investigators showed fairly constant optical properties and closely related chemical composition; however, these workers anticipated that other clay minerals of micaceous origin might be discovered with somewhat different properties, thus requiring new names to describe the variants and some broadening of the significance of the term "illite" as a group name.

The present authors feel that it would be premature to advance the claim that the "x" mineral, found in California soil colloids, properly belongs to the

TABLE 20
Theoretical interplanar spacings for clay minerals

KAOLINITE [GRUNER (14)]			MONTMORILLONITE [MAEGDEFRAU AND HOFMANN (27)] (AT ROOM TEMPERATURE)			ILLITE [GRIM, BEAY AND BRADLEY (13)]		
Spacing d	Intensity	Miller indexes	Spacing d	Intensity	Miller indexes	Spacing d	Intensity	Miller indexes
Å.			Å.			Å.		
7.14	10	(002)	ca. 14-15	v.v.s.	(001)	9.98	s.	(002)
			ca. 5	Variable	(003)	4.97	w.	(004)
4.397	6	(110) (11 $\bar{1}$)	4.49	v.s.	(110) (020)	4.47	s.	(110)
4.248	3	(021)						
						4.11	v.w.	(022)
3.570	10	(004)				3.7	v.w.	(023)
						3.40	v.w.	(11 $\bar{4}$)
*3.33	Indis- tinct	(11 $\bar{3}$)				*3.31	m.	(006)
			ca. 3.0	Variable	(005)	3.2	v.w.	(114)
						2.98	w.	(025)
						2.84	v.w.	(115)
{2.582	5	(114) (11 $\bar{5}$)	2.59	s.	(130) (200)	2.56	v.s.	(20 $\bar{2}$)
{2.48	5	(131) (132)						
						2.44	w.	(13 $\bar{3}$)
2.38	2	(006)				2.38	m.	(133)
2.343	8	(132) (13 $\bar{3}$)						
2.261	4	(202) (20 $\bar{4}$)	2.24	v.w.	(220) (040)	2.24	m.	(22 $\bar{1}$)
						2.18	w.	(22 $\bar{3}$)
						2.11	w.	(043)
{2.015	4	(222) (22 $\bar{4}$)						
{1.987		(134)				1.98	m.	(0010)
1.826	2	(13 $\bar{6}$)						
{1.671		(240) (24 $\bar{2}$)	1.70	m.	(240) (310) (150)			
{1.669	7	(136) (137)						
{1.665		(151) (152)				1.65	w.	(1310)
						1.64	m.	(312)
1.530	3	(137) (13 $\bar{8}$)						
			1.495	s.	(330) (060)	1.50	s.	(060)
{1.483	8	(060)						
{1.481		(332)						
1.465	2	(33 $\bar{3}$)						
						1.34	v.w.	(335)
1.297	4	(1, 3, 1 $\bar{0}$)	1.30	w.	(260) (400)	1.29	m.	(400)
1.235	3		1.245	w.	(420) (350) (170)	1.24	w.	(0016)

* Quartz (101) spacing = 3.34 v.v.s.

Adjacent spacings bracketed together signify a broad band extending over the indicated range, instead of a sharp line.

Symbols for the intensities of the x-ray reflections: v.s. = very strong; s = strong; m.s. = medium strong; m. = medium; w-m. = weak to medium; w. = weak; v.w. = very weak; v.v.w. = very, very weak; tr. = trace; ? = doubtful.

illite group. So far no attempt has been made to isolate it by methods similar to those employed by Grim and his co-workers; hence it has not been possible to compare either the optical properties or the chemical composition of these materials with that given for illite. The x-ray patterns of the California colloids, however, contain lines which agree well with the lines reported for illite, and this suggests rather strongly that an important constituent of these colloids is a clay mineral belonging to or closely related to this group.

It should be evident from the foregoing discussion that present knowledge does not warrant definite conclusions as to the exact spacings of the "x" mineral found in California soils. Since these colloids may prove to fit into the illite classification, however, it is interesting to compare their interplanar spacings with those which have been established for illite. Again we advance the principle, set forth in our previous paper (25), that only spacings which can be indexed with respect to an established unit cell are acceptable as reference spacings. The list of spacings given by Grim et al. (13) for illite essentially meets this requirement. Although these authors do not give definite lattice dimensions for illite, they have presented a set of interplanar spacings for that mineral in comparison with the spacings calculated for muscovite from the data of Jackson and West (19). As the interplanar distances differ only slightly, Grim et al. concluded that the illite crystal cell is almost like the muscovite cell, differing from it by being only about one-third per cent shorter in the direction of the *c* axis. The numerical differences between the values for the interplanar spacings for muscovite and illite are so slight that the spacings for each may be assigned the same indexes with but little likelihood of error. The lines of the illite structure appear to be the most satisfactory set of reference lines now available for comparison with the "x" mineral of California soil colloid.

The lines in the patterns of many soil colloids are more or less diffuse because of the presence of considerable very finely divided material, which tends to produce broadened lines, or because of the presence of noncrystalline material, which tends to produce undue darkening of the background. In addition, as seen from the tables, nearby lines tend to overlap, even in the pattern of only a single mineral; when two or three different clay minerals are present, the overlapping may be much greater. Accordingly, an attempt to identify all of the lines in a soil colloid pattern is attended with many uncertainties.

Fortunately, it is usually possible to identify the clay minerals by the wide spacings, disregarding entirely the rest of the pattern. Thus with air-dried material the 14-15Å. spacing is characteristic of the montmorillonitic group of clays; the 10Å. spacing, of the "x" mineral; and the 7Å. spacing, of the kaolinitic group. The exact numerical values of these spacings, as ordinarily determined, vary slightly, partly because of lack of refinement in technic and perhaps partly because each of the three clay mineral types may be represented by several individual minerals having slightly different lattice constants. The variation among these values is not wide, however, and in no case is it likely to lead to erroneous identification.

The identification, made on the basis of the wide spacings, may be confirmed by examining the same materials after heating to 500° for some hours. In the pattern of the heated materials, the characteristic montmorillonite line is in a new position corresponding to a spacing of about 9.5-10Å.; the 7Å. line, characteristic of unheated kaolinite, is entirely absent; and the 10Å. line, characteristic of the "x" mineral, remains unchanged.

As has been indicated in this paper under the discussion of optical properties, when soil colloids are separated by decantation, the clay particles tend to form aggregates and to entangle mineral fragments of varying sizes. Correspondingly, the x-ray diffraction patterns of nearly all the colloids that we have examined give evidence of the presence of minerals other than the three clay types. Outstanding among these is quartz, which is almost invariably present.

TABLE 21
Theoretical interplanar spacings for important mineral inclusions

ALPHA QUARTZ			ZIRCON			RUTILE		
Spacing	Intensity	Miller indexes	Spacing	Intensity	Miller indexes	Spacing	Intensity	Miller indexes
Å.			Å.			Å.		
			{ 4.65	m.s.	(110)			
			{ 4.40		(101)			
4.25	m.	(100)						
			{ 3.66	v.s.	(111)			
3.34	v.v.s.	(101)	{ 3.29		(220)			
						3.24	v.s.	(110)
2.45	m.	(110)	2.50	s.	(112)	2.48	s.	(101)
2.28	m.	(102)	2.33	w.	(220)	2.29	w.	(200)
{ 1.81	m.s.	(112)						
{ 1.80		(003)						
			1.74	v.s.	(231)			
1.67	m.	(202)				1.68	v.s.	(121)
1.54	s.	(121)				1.62	s.	(220)
1.38	v.s.	(122)	1.41	s.	(114)	1.42	w.	(221)

Optical evidence has been noted for the occurrence of zircon, rutile, and iron oxide. As will be shown later, the x-ray data confirm the optical evidence. Quartz, zircon, and rutile give characteristic x-ray patterns, and, even in complex mixtures, it is sometimes possible to recognize lines produced by spacings in these minerals.

Two forms of quartz have been recognized by crystallographers, and crystal structures have been assigned to each. The alpha form is stable at temperatures below 573°, and the beta form exists at temperatures between 573° and 870°. According to Bragg (4, p. 84) the alpha-beta transformation of quartz takes place rapidly and is reversible. According to Dana and Ford (9, p. 471), alpha quartz occurs in geodes and veins, whereas the beta modification was the original form in granites and porphyries.

In table 21 are given the interplanar spacings for the strongest x-ray re-

TABLE 22
Interplanar spacings of the Yolo colloids

MINER- ALS*	431		7083		17557		17558		17559	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
M	15.4 s.	10.1 m.s.	15.3 s.	10.1 w.	15.2 s.	10.0 w-m.	15.4 s.	10.0 w.	15.3 s.	10.1 w.
K					7.3 m.		7.3 v.w.		7.3 v.w.	
M	4.49 s.	4.5 s.	4.5 s.	4.5 s.	4.5 s.	4.5 s.	4.5 s.	4.45 m.s.	4.5 s.	4.5 s.
Q	3.35 w-m.	3.35 m.	3.36 s.	3.4 w.	3.33 s.	3.35 s.	3.32 s.	3.35 s.	3.32 m.	3.35 s.
M	3.15 w-m.	3.20 w-m.			3.2 v.w.		3.18 v.w.	3.20 w.	3.23 w.	3.20 w.
MK	2.60 s.	2.60 w.	2.57 s.	2.63 m.	2.57 s.	2.62 m.	2.59 s.	2.60 m.s.	2.57 m.s.	2.62 s.
	2.56	2.52		2.50			2.52			2.56
Q	2.45 w.	2.42 v.w.		2.45 w.	2.43 m.	2.45	2.41 w.	2.45 m.s.		2.45 w.
MK			2.13 w.	2.25 w-m.				2.30 s.		2.27 w.
U	2.13 w.							2.16 m.		
KQ			1.83 w.		1.82 w.	1.82 w.	1.82 w.	1.83 s.		1.82 w.
MQ	1.70 m.	1.70 w.	1.70 w.	1.70 v.w.	1.71 w.	1.70 w.	1.72 w.	1.68 m.	1.69 v.w.	1.70 w.
K	1.64	1.66	1.66		1.64	1.66	1.65			1.68
KQ	1.53 v.w.	1.53 w-m.	1.50 m.s.	1.53 m.	1.54 w.	1.54 m.s.	1.53 m.	1.55 s.	1.53 w.	1.54 s.
M	1.50 m.	1.50	1.50 m.s.	1.50	1.50 m.s.	1.50	1.49 s.	1.52 w.	1.49 s.	1.50
Q						1.37 w-m.		1.39 s.		1.38 s.
MK	1.29 v.w.	1.29 v.w.	1.29 w.	1.30 w.	1.295 w.	1.30 w.	1.29 w.	1.30 v.w.	1.29 w.	1.30 w.
MK						1.25 w.		1.26 w-m.		1.25 w.

* Symbols for minerals: I = "x" mineral; K = kaolinite; M = montmorillonite; Q = quartz; R = rutile; Z = zircon; U = unidentified mineral. These letters signify that the particular line in the pattern might be due to the indicated mineral, not that the presence of the mineral is necessarily established by the line.

flections of alpha quartz and of zircon and rutile. The numerical values for these spacings have been calculated from the unit cell dimensions for these minerals, as recorded by Bragg (4). The visual intensities of the reflections, as given in the table, were observed by the present authors on diffraction patterns made from authentic samples of the respective minerals. Account is taken of only a few of the strongest lines for each mineral, since only these are of value for identification in mixtures.

In the following sections are given the findings for the different series of colloids discussed in this paper. In general, the clay minerals were identified by the data presented in the odd-numbered tables, which give only the wide

TABLE 23
Effect of partial dehydration on interplanar spacings of Yolo colloids

SAMPLE NUMBER	TEMPERATURE	MONTMORILLONITE SPACINGS	KAOLINITE SPACINGS
		Å.	Å.
431	25	15.4	None
	100	15.2	None
	300	10.7	None
	500	10.1	None
7083	25	15.3	None
	100	14.5	None
	300	10.3	None
	500	10.1	None
17557	25	15.3	7.3
	500	10.0	None
17558	25	15.4	7.3 v.w.
	100	14.5	7.3 v.w.
	300	11.6	7.3 v.w.
	500	10.0	None
17559	25	15.3	7.3
	500	10.1	None

Note: No "x" mineral spacings found in any of these samples.

spacings and the effect upon them of partial dehydration. Confirmation was then sought from the complete list of spacings found in the even-numbered tables, and these lists were then scrutinized for evidence of quartz and other inclusions.

Yolo clay colloids. The data in tables 22 and 23 show that the Yolo samples are preponderantly montmorillonitic. All the 25° samples showed a strong spacing of 15.2 to 15.4 Å., whereas the samples heated to 500° showed a 10 Å. spacing. Furthermore, the samples heated to 100° and 300°, respectively, showed spacings intermediate between the 15 and 10 Å. values. These spacings all correspond to the characteristic spacing in montmorillonite, designated

by Hofmann, Endel, and Wilm (18) as the (001) spacing, which varies according to heat treatments. In the Davis colloids (samples 17557-17559), the presence of a 7.3Å. spacing in the 25° samples and its absence in the samples that were heated to 500°, affords definite evidence of kaolinite or related minerals. Neither the La Habra (sample 431) nor the Gilroy (sample 7083) Yolo clay colloid gave a 7Å. spacing, from which it may be concluded that kaolinitic material is not present in significant quantity in these colloids. None of the unheated Yolo colloids gave a 10Å. spacing; hence no important quantity of the "x" material was present.

TABLE 24
Interplanar spacings of the Vina colloids

MINER-ALS*	16054		16055		16056	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
	Å		Å.	Å.	Å.	Å.
M		No pattern	ca. 15 ?		15.4 v.w.	
K	7.3 m.	No pattern	7.3 m.	7.3 w.	7.24 m.	ca. 7 v.v.w.
U	5.95 v.v.w.	No pattern	5.9 w.			
U	5.4 ?	No pattern	5.4 w.			
MKI	4.5 s.	No pattern	4.45 s.	4.5 m.	4.45 s.	4.45 s.
U		No pattern			4.05 v.w.	4.05 w.
K	3.6	No pattern	3.6 m.		3.6 w.	
Q	3.3	No pattern	3.32 w-m.	3.35 w.		
M		No pattern			3.18 w.	3.21 w.
K	2.57 m.	No pattern	2.58 s.	2.57 w.	2.60 m.s.	
K		No pattern			2.50	2.51 w.
K		No pattern	2.35 w.		2.32	
K		No pattern	2.20 w.			
Q	1.69 m.	No pattern	1.69 m.	1.68 v.w.	1.69 m.	1.69 m.
MK	1.50 m.	No pattern	1.50 s.		1.50 s.	1.50 w.
K	1.275 v.w.	No pattern	1.29 v.w.		1.295 v.w.	
K		No pattern	1.24 v.w.		1.24 v.w.	

* See footnote table 22.

Quartz was present in all of the Yolo samples, as shown by the distinct 3.32-3.36Å. spacing, which represents the strongest reflection of quartz. Supplementary evidence is furnished by the 2.45, 1.82, 1.54, and 1.38 spacings found in most of the patterns.

Vina clay colloids. The Vina clays were, in general, rather less crystalline than the other colloids that have been examined. The patterns obtained from this series showed considerable general darkening of the background, and the diffraction lines were, in some instances, difficult to distinguish. All three samples show definitely the presence of the 7Å. spacing in the unheated materials (table 24). In one instance this spacing disappeared on heating to 500°; in the other two, the intensity of its reflection was much diminished

(table 25). These observations indicate the presence of kaolinitic material as the predominating clay mineral. Two of the samples showed the presence of a weak 15\AA . line in the unheated form. This suggests that a small amount of montmorillonitic material was probably also present. No evidence for the presence of the "x" mineral was found. Quartz was present in small amounts.

In view of the small number of Vina samples that have been studied and of their poorly crystalline character, the conclusions from the x-ray data should be accepted with some reserve.

Keefers clay colloids. The tabulation of wide spacings given in table 27 shows that the only clay mineral present in recognizable quantity was of the kaolinitic type. The complete list of spacings in table 26 supports this finding, in that the patterns obtained from the heated materials show only a few spacings remaining after the thermal destruction of the kaolinite crystal

TABLE 25
Effect of partial dehydration on interplanar spacings of Vina colloids

SAMPLE NUMBER	TEMPERATURE	MONTMORILLONITE SPACINGS	KAOLINITE SPACINGS
	°C.	Å.	Å.
16054	25	None	7.3
	100	None	7.3
	300	None	7.3
	500	None	None
16055	25	ca. 15 ?	7.3
	100	13.8 ?	7.3
	300	None	7.3
	500	None	7.3 w.
16056	25	15.4 v.w.	7.25
	500	None	ca. 7 v.v.w.

Note: No "x" mineral spacings found in any of these samples.

structure. These remaining spacings, of rather weak intensity, are not related to the patterns of the clay minerals; they are rather to be ascribed to quartz and possibly to zircon and other mineral inclusions, thus supporting the optical evidence for the presence of these minerals.

Sierra clay colloids. The data in table 29 show that all four horizons of the Mount Orcum profile gave patterns containing the strong 7\AA . kaolinite line, which disappeared when the samples were heated to 500° . This establishes the essentially kaolinitic nature of these colloids. In addition, all the samples showed the presence of a weak 10\AA . line. The presence of this line was certain, however, only in material which had been heated to 500° , and, from the wide spacing data of table 29, this spacing could be due to either montmorillonite or the "x" mineral. Confirmatory evidence for the presence of montmorillonite would be a stronger 15\AA . spacing in the unheated material. Sam-

ple 16309 showed a feeble indication of a montmorillonite spacing when heated to 100°C. and a doubtful indication of the "x" mineral in the unheated

TABLE 26
Interplanar spacings of the Keefers colloids

MINERALS*	16057		16058	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°
	Å	Å.	Å.	Å.
K	7.25 m.s.		7.25 m.	
Z		4.60 w.		
K	4.40 m.s.		4.40 s.	4.45 m.
K	4.25 v.w.			
Z		3.80 ?		
K	3.52 m.		3.55 m.	
Z		3.40 w.		
Q	3.32 m.		3.33 w-m.	3.33 m.
K	2.58 m.		2.57	
Z		2.53 m.		2.51 w.
K	2.50		2.48	
K	2.34 w.		2.35 w-m.	
U	2.20 v.w.	2.20 v.w.	2.20 w.	
K	1.97 v.w.			
KQR	1.70 w.	1.69 w.	1.69 m.	1.70 w.
K	1.66			
Q	1.535 v.w.	1.55 v.w.		
U	1.49 m.s.	1.46	1.49 s.	
Q	1.37 v.v.w.			
K	1.29 v.v.w.		1.295 v.v.w.	
K	1.24 v.v.w.		1.23 v.v.w.	

* See footnote table 22.

TABLE 27
Effect of partial dehydration on interplanar spacings of Keefers colloids

SAMPLE NUMBER		TEMPERATURE	KAOLINITE SPACINGS
		°C.	Å.
16057	{	25	7.25
		100	7.3
		300	7.3
		500	None
16058	{	25	7.25
		500	None

Note: No montmorillonite or "x" mineral spacings found in any of these samples.

material. In the other three samples of this profile confirmatory evidence of montmorillonitic material is entirely lacking. Accordingly a decision as to

TABLE 28
Interplanar spacings of the Sierra colloids

MINERALS*	16308		16309		16310		16311	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
I	Å.	Å.	Å.	Å.	Å.	Å.	Å.	Å.
K	7.25 m.s.	10.3 w.	10.1 ?	10.1 w.	7.3 m.s.	10.1 w.	7.25 s.	10.1 v.w.
U			7.30 m.s.					
IZ			5.90 w.					
IZ								
KZ	3.59 s.	4.55 s.	4.45 s.	4.5 s.	4.5 s.	4.45 m.	4.45 v.s.	4.5 v.w.
Q	3.33 w.	3.33 w.	3.62 m.s.				3.60 s.	
U				3.32 w-m.			3.35 w.	3.35 v.w.
KI				2.62 v.w.			2.72 tr.	2.70 v.w.
KIZ	2.62 m.	2.60 w.	{ 2.60 w.	2.53 v.w.			{ 2.60 m.	
R	2.52 m.	2.52 w.	{ 2.50 w.		2.50 m.		{ 2.50	2.50 v.w.
IQ				2.42 v.w.				
KI	2.39 w.	2.43 w.			2.37 w.			
K	2.32 w-m.		2.34 w.				2.35 w-m.	
Q		2.27 v.w.						
Q	2.17 v.w.	2.17 v.w.	2.17 v.w.	2.17 w.			2.18 w.	2.20 v.w.
I								
KI	1.98 w.	1.98 v.w.	1.99 w.		2.16 v.w.			
U		1.89 v.w.						
Q		1.83 v.v.w.						
KQR	{ 1.69 m.s.	1.68 v.v.w.	1.68 w-m.	1.83 w.				1.83 w.
	{ 1.66			1.68 w.	1.68 m.	1.68 w-m.	{ 1.72 m.	1.69 w-m.
KQ							{ 1.66 m.	
KI	1.53 m.s.	1.53 w.	1.53 w.	1.53 w.	1.53 v.w.	1.53 v.w.	1.53 w.	1.53 w.
U	1.485 s.		1.50 m.	1.50 w.	1.50 m.	1.49 v.w.	1.50 s.	1.50 w.
KI							1.47 v.w.	1.45 w.
KI	1.285 v.w.						1.29 v.w.	1.29 v.w.
KI	1.235 v.w.						1.24 w.	1.24 v.w.

* See footnote table 22.

the clay minerals present, other than kaolinite, cannot be made on the basis of the wide spacing tabulated in table 29.

The complete tabulation of all spacings, as given in table 28, affords more convincing evidence, especially the spacing obtained from the material heated to 500°. After the destruction of the kaolinite structure by heating, the remaining simplified pattern contains several lines which correspond with the reference spacing of the "x" mineral rather than with those of montmorillonite. Other spacings characteristic of quartz, zircon, and rutile, as well as unidentified spacings, are found in the patterns from the 500° samples. These results are consistent with the optical observations on the Sierra clays.

Redding clay colloids. A spacing of about 7Å. was found in all thirteen of the air-dried Redding samples (tables 30a, 30b, 30c) but was absent from the samples when heated to 500°. This establishes the presence of kaolinite or

TABLE 29
Effect of partial dehydration on interplanar spacings of Sierra colloids

SAMPLE NUMBER	TEMPERATURE	MONTMORILLONITE SPACINGS	KAOLINITE SPACINGS	"X" MINERAL SPACINGS
	°C.	Å.	Å.	
16308	25	None	7.25	None
	500	None	None	10.3
16309	25	None	7.3	10.1 ?
	100	14.8 (v.w.)	7.3	None
	300	None	7.3	None
	500	None	None	10.1
16310	25	None	7.3	None
	500	None	None	10.1
16311	25	None	7.25	None
	500	None	None	10.1

related minerals in all of the Redding colloids. The 15Å. spacing, characteristic of montmorillonite, was observed in five of the thirteen samples, but in only two of them was the corresponding spacing of about 9.5–10Å. found after the samples were heated to 500°. In only two instances was a strong montmorillonite line observed in the Redding clays, namely, samples 16315 and 16316 from Palermo. The 10Å. spacing, characteristic of the "x" clay mineral, was not observed in any of the Redding clays.

The x-ray data indicate, therefore, that the Redding clays are preponderantly kaolinitic but that certain samples also contain significant amounts of montmorillonite or similar minerals (table 31). The Oroville clays (samples 16317 and 16318) and all except one horizon of the Kearney Mesa and one horizon of the Olinda samples appear to be virtually free from montmorillonitic material. The clay from all three horizons of the Palermo

TABLE 30a
Interplanar spacings of the Redding colloids—Kearney Mesa

M N K	16303		16304		16305		16306		16307	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
M	Å.	Å.	Å.	Å.	Å.	Å.	Å.	Å.	Å.	Å.
K	7.25 m.		7.4 m.		7.4 w-m.		15.2 w. 7.3 s.		7.3 w.	
KM	4.45 m.	4.50 s.	4.4 s.	4.5 v.s.	4.45 m.s.	4.45 m.	4.45 v.s.	4.5 s.	4.45 m.s.	4.5 m.s.
K	3.55 m.		3.53 m.		3.52 m.		3.60 s.		3.60 m.	
Q	3.33 m.	3.37 s.	3.32 m.	3.37 s.	3.33 m.	3.35 m.s.	3.35 m.	3.35 s.	3.35 w-m.	3.35 s.
U					2.72 w.	2.72 w-m.		2.72 w-m.		
KM	{ 2.60 w-m. 2.52	{ 2.56 w. 2.50	{ 2.60 m. 2.52	{ 2.60 m. 2.50	{ 2.60 m. 2.52	2.52 w-m.	{ 2.60 m.s. 2.50	{ 2.60 w. 2.50	{ 2.60 m. 2.52	{ 2.60 m. 2.52
K	2.37 w.		2.36 w.				2.38 m.s.	2.32 w.		
U					2.19 v.w.		2.22 v.w.			
K	1.99 v.w.		1.98 v.w.		1.96 v.v.w.					
KQ	1.83 v.w.	1.83 w.	1.83 v.w.	1.83 w.	1.83 v.w.	1.84 v.w.		1.86 w.		
KQ	1.69 m.	1.69 w.	{ 1.70 w. 1.66	{ 1.70 w. 1.67	{ 1.70 w-m. 1.66	1.69 v.w.	{ 1.71 s. 1.67	1.70 w.	1.68 w.	1.68 w.
Q										
KQ	1.49 s.		1.495 s.	{ 1.52 w. 1.50	1.49 m.s.		1.50 v.s. 1.45 w.	1.50 w. 1.45 w.	1.49 w.	1.49 w.
Q							1.39 w.			
Q	1.38 v.w.		1.38 v.w.	1.37 w.			1.29 m.		1.37 v.w.	1.37 v.w.
K	1.29 v.w.		1.29 v.w.	1.29 v.w.	1.29 v.w.		1.24 m.			
K	1.24 v.w.		1.24 v.w.	1.25 v.w.	1.24 v.w.					

* See footnote table 22.

TABLE 30b
Interplanar spacings of the Redding colloids—Sacramento Valley

MIN- ERALS*	PALERMO						OROVILLE			
	16314		16315		16316		16317		16318	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
M	15.2 ?	Å.	15.2 s.	9.6 v.w.	15.0 s.	Å.	7.8 w.	Å.	7.25 w.	Å.
K	7.4 m.		7.4 m.s.		7.4 m.					
U	5.8 w.									
KM	4.45 s.	4.45 w.	4.5 w.	4.45 s.	4.45 v.s.	4.45 s.	4.40 s.	4.45 s.	4.45 s.	4.50 s.
Q	4.1 w.						4.20 w.		4.25 w.	
U								3.75 w.		
K	3.58 m.s.		3.55 m.	3.35 v.w.	3.58 m.s.	3.30 w.	3.57 w.	3.35 v.s.	3.50 w.	3.35 v.s.
Q	3.32 s.	3.33 w.					3.32 s.	2.70 m.s.	3.33 s.	2.70 m.
U	2.68 m.						2.67 w.			
KM	2.60 m.		2.60 s.	2.60 m.s.	2.60 v.s.	2.60 m.	2.60 m.		2.60 w-m.	
Q	2.50	2.51 w.	2.52	2.50	2.50	2.50	2.50		2.50	2.53 s.
K	2.36 m.		2.35 m.		2.37 m.		2.32 w.		2.35 w.	2.22 w-m.
U							2.21 v.w.	2.23 s.		
K	1.98 v.w.						1.97 v.w.			
U	1.92 v.v.w.						1.91 v.w.			
K	1.83 v.w.						1.82 v.w.	1.83 m.s.	1.82 v.w.	1.83 m.
KM	1.71 w.	1.69 v.w.	1.69 w.	ca. 1.70 v.w.	1.71 m.	1.68 w.		1.69 s.	1.68 w-m.	1.70 m.s.
	1.66				1.67					
KQ							1.54 w.			1.52 s.
KM	1.49 s.		1.50 v.s.	ca. 1.50 w.	1.50 v.s.	1.50 m.s.	1.50 s.	1.49 w.	1.49 s.	
K	1.46 v.w.						1.45 m.	1.45 w-m.	1.46 v.w.	1.46 v.w.
Q	1.38 w.						1.37 w-m.	1.38 m.	1.37 v.v.w.	1.38 v.w.
K	1.29 v.w.		1.29 w.		1.29 m.		1.29 v.w.	1.31 v.w.	1.29 v.v.w.	
K	1.24 v.w.		1.24 v.w.		1.24 m.		1.24 v.w.	1.26 v.w.	1.235 v.v.w.	1.26 v.w.

* See footnote table 22.

profile (samples 16314-16316) gave x-ray indications of the presence of montmorillonite which were especially strong in the 20-40-inch horizon (sample 16315). This is an interesting confirmation of the chemical and optical data reported above.

TABLE 30c
Interplanar spacings of the Redding colloids—Olinda

MINERALS*	16319		16320		16321	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
	Å.	Å.	Å.	Å.	Å.	Å.
M	15.0 w.					
K	7.3 s.		7.25 s.		7.25	
KM	4.5 s.	4.5 s.	4.40 v.s.	4.50 s.	4.40 v.s.	4.45 s.
K	4.25 w.		4.20 w.		4.25 v.w.	
U				3.70 v.w.		
K	3.58 m.s.		3.57 m.		3.58 m.	
Q	3.35 m.s.	3.35 s.	3.31 m.	3.35 s.	3.32 w.	3.32 s.
U	2.70 w.	2.70 s.	2.70 w.	2.70 s.	2.70 w.	2.70 m.s.
K	2.62 s.		2.60 m.s.		2.60 m.s.	
U	2.52	2.52 s.		2.52 v.s.		2.52 s.
K			2.50		2.50	
K	2.37 m.		2.37 m.		2.37 m.	
U	2.22 w.		2.20 w.	2.20 w-m.	2.21 w.	2.21 w-m.
K	2.00 w.		1.98 v.w.		1.98 v.w.	
U						1.87 v.w.
KQ	1.85 w.	1.82 w.	1.83 v.w.	1.83 m.	1.83 v.w.	1.82 w.
KQ	1.72 w.		1.70 m.s.	1.70 m.s.		1.70 s.
KQ	1.68	1.68 m.s.	1.66			
U		1.58 w.				
K	1.53 w.		1.54 v.w.			
K	1.50 v.s.		1.49 s.	1.49 m.		1.50 w-m.
K	1.47 w.		1.46 w.			
Q		1.43 w-m		1.45 m.		1.45 w-m.
Q	1.39 w.	1.38 v.w.	1.38 v.w.	1.38 w.		1.38 w.
K	1.29 v.w.		1.29 v.w.	1.29 v.w.		1.29 v.w.
K	1.24 w.	1.24 v.w.	1.24 v.w.	1.24 v.w.		1.24 v.w.

* See footnote table 22.

Most of the Redding samples gave evidence of quartz. Unidentified spacings point to the presence of other inclusions but furnish no clue to their identity.

San Joaquin clay colloids. All the x-ray diffraction patterns obtained from the samples of the San Joaquin soils showed the 10Å. spacing characteristic of the "x" mineral, and all patterns also showed the 7Å. spacing of kaolinite, which disappeared in every case except one upon heating to 500°C. (table 33). The disappearance of this spacing on heating definitely confirms the presence

TABLE 31

Effect of partial dehydration on interplanar spacings of Redding colloids

SAMPLE NUMBER		TEMPERATURE	MONTMORILLONITE SPACINGS	KAOLINITE SPACINGS
		°C.	Å.	Å.
16303	{	25	None	7.25
		500	None	None
16304	{	25	None	7.4
		100	None	7.4
		300	None	7.4
		500	None	None
16305	{	25	None	7.4
		500	None	None
16306	{	25	15.2	7.3
		500	None	None
16307	{	25	None	7.3
		500	None	None
16314	{	25	15.2	7.4
		500	None	None
16315	{	25	15.2	7.4
		500	9.6	None
16316	{	25	15.0	7.4
		500	9.8	None
16317	{	25	None	7.3
		500	None	None
16318	{	25	None	7.25
		500	None	None
16319	{	25	15.0	7.3
		500	None	None
16320	{	25	None	7.25
		500	None	None
16321	{	25	None	7.25
		500	None	None

Note: No "x" mineral spacings found in any of these samples.

of kaolinitic material, the single exception of a weak reflection being ascribed to incomplete heat treatment. The 15Å. line characteristic of montmorillonite was not found in any pattern of the San Joaquin colloids. The

data, therefore, definitely establish that the clay minerals of the San Joaquin soils are of the kaolinitic and the "x" mineral types, and that the montmorillonitic type is absent.

The more detailed data of tables 32a and 32b indicate that most of the spacings in the patterns of the San Joaquin clays may be identified with kaolinite and the "x" mineral. Quartz spacings were also present in all of the patterns.

TABLE 32a
Interplanar spacings of the San Joaquin colloids—Fairmead and Pixley Area

MINERALS*	6530		18882		18883	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
	Å.	Å.	Å.	Å.	Å.	Å.
I	10.0 m.	10.0 m.	10.1 w.	10.1 w.	10.1 w.	10.1 w.
K	7.25 w.		7.3 m.	7.3 w.	7.4 w.	
KI	4.42 s.	4.5 m.	4.45 m.	4.50 s.	4.45 s.	4.5 s.
Q					4.25 w.	
K					3.57 w.	
Q	3.32 s.	3.35 s.	3.35 m.	3.35 s.	3.33 s.	3.35 v.s.
I		2.95 w.				
KI	2.59 s.	2.62 m.	2.60 m.	2.60 s.	2.60 m.	2.60 v.s.
I					2.54	2.52 w-m.
I	2.42 w.	2.44 m.	2.42 w.	2.45 m.	2.42 w.	2.44 m.
KI			2.27 w.			2.25 w-m.
I	2.17 w.	2.17 m.	2.17 w.	2.17 w.	2.18 w.	2.17
KI	1.98 w.		2.00 v.w.	2.00 w.	2.00 v.w.	1.98 w-m.
KQ				1.82 w.	1.82 v.w.	1.82 w.
KQ	1.69 m.	1.68 w.	1.68 w.	1.70 m.	1.68 w.	1.70 m.
KI	1.66			1.66		1.66
Q	1.53 m.	1.53 s.	1.53 w.	1.53 m.s.	1.54 m.	1.53 s.
I	1.50 m.			1.50 m.s.	1.50 m.	1.50
Q	1.36 w.			1.37 w.	1.37 w.	1.37 v.w.
KI	1.30			1.30 v.w.	1.29 w.	1.29 v.w.
KI					1.24 v.w.	1.24 v.w.

* See footnote table 22.

A few spacings were not identified. No evidence was found for the presence of either zircon or rutile.

Hanford clay colloids. All patterns obtained from the Hanford samples showed the 10.0Å. spacing, indicating that the predponderant clay mineral was the "x" mineral (tables 34 and 35). The presence in the Van Nuys sample (No. 7095) of a small proportion of montmorillonite was indicated by a faint reflection of the 15Å. spacing in the air-dried material. The correspond-

TABLE 32b
Interplanar spacings of the San Joaquin colloids—Terra Bella and Lindcove

MINERALS*	18884		18885		18888		18889	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
I	\bar{A} .	\bar{A} .	\bar{A} .	\bar{A} .	\bar{A} .	\bar{A} .	\bar{A} .	\bar{A} .
K	10.0 w-m.	10.0 w-m.	10.0 w-m.	10.0 s.	10.2 w.	10.1 w.	10.0 w.	10.0 m.
KI	7.25 w-m.		7.25 w-m.		7.25 w.		7.25 m.	
K	4.50 s.	4.5 m.s.	4.45 v.s.	4.45 s.	4.50 m.	4.50 m.s.	4.45 v.s.	4.50 s.
K	4.40 w.							
K	3.35 v.s.	3.35 s.	3.35 s.	3.35 v.s.	3.35 m.s.	3.35 v.s.	3.57 s.	3.35 v.s.
Q			3.20 w.				3.35 v.s.	
I								
I								
U							2.95 w-m.	
KI	2.63 s.	2.62 m.	2.58 v.s.	2.63 m.s.	2.63 m.	2.60 m.	2.57 s.	2.66 m.s.
I	2.58	2.50		2.50 w.		2.52 w.		2.53 m.
I	2.46 m.	2.43 m.	2.43 m.	2.43 m.	2.43 w-m.	2.43 m.		2.50 w.
U								
Q				2.25 w.		2.29 w.		2.39 w.
I	2.17 w-m.		2.18 w.	2.17 w.	2.17 w.	2.17 w-m.	2.17 m.	2.30 v.w.
KI	2.00 w.		2.00 m.	1.98 w.	2.00 w.	1.99 w.	1.99 w-m.	2.22
U					1.90 v.w.	1.82 w.	1.87 w.	1.90 v.w.
Q	1.83 w.	1.83 m.	1.82 w.	1.82 w-m.	1.83 v.w.	1.82 w.	1.82 w.	1.83 v.w.
KQ	1.72 m.s.		1.70 s.	1.68 m.s.	1.68 w.	1.68 m.	1.70 s.	1.68 v.w.
KI	1.66	1.67 m.	1.66				1.64	
Q	1.54 m.s.	1.54 s.	1.53 m.s.	1.53 s.	1.54 s.	1.54 m.s.	1.54 m.s.	1.54 m.s.
I	1.50 s.		1.50 s.	1.47 ?	1.50 s.		1.48 v.s.	
Q	1.39 m.	1.385 m.	1.37 m.	1.38 m.	1.37 w.	1.37 v.w.	1.38 w.	
KI	1.29 v.w.		1.29 v.w.	1.32 v.w.		1.32 v.w.		
KI	1.24 v.w.		1.24 v.v.w.	1.26 v.w.		1.26 v.w.		

* See footnote table 22.

ing 9.5Å. spacing could not be recognized in the material heated to 500°; this is not surprising, as the reflection from the heated material is usually much more diffuse than that from the unheated material. Moreover, this line would be difficult to observe because of its proximity to the 10Å. spacing of the "x" mineral. The "x" mineral was apparently the only clay mineral in the Delano sample (No. 18886). A 7.25Å. spacing in the patterns from the lower temperature Exeter samples (No. 18887), but absent from the 500°

TABLE 33

Effect of partial dehydration on interplanar spacings of San Joaquin colloids

SAMPLE NUMBER	TEMPERATURE	KAOLINITE SPACINGS	"X" MINERAL SPACINGS
		Å.	Å.
6530	25	7.25	10.1
	100	7.3	10.2
	300	7.3	10.1
	500	None	10.1
18882	25	7.3	10.3
	100	7.3	10.1
	300	7.3	10.3
	500	7.3 w.	10.0
18883	25	7.4	10.1
	500	None	10.1
18884	25	7.25	10.0
	500	None	10.0
18885	25	7.25	10.0
	500	None	10.0
18888	25	7.25	10.2
	500	None	10.1
18889	25	7.25	10.0
	500	None	10.0

Note: No montmorillonite spacings found in any of these samples.

sample, definitely identifies a kaolinitic mineral in addition to the "x" mineral. No montmorillonite spacing was found in this sample.

The complete list of spacings in table 34 shows the presence of quartz in all of the Hanford samples. The probable presence of other mineral inclusions was indicated by several spacings not identified with any known minerals.

Various clay colloids. Inasmuch as the Madera, Tujunga, Ramona, Placentia, and Maxwell soils were represented by a single sample each, and the Tule soil by a single profile, it is not desirable to draw broad conclusions from the x-ray data. Even the tabulation showing the effect of dehydration on

TABLE 34
Interplanar spacings of the Hanford colloids

MIN- ERALS*	7095		18886		18887	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
	Å.	Å.	Å.	Å.	Å.	Å.
M	15.5 w.					
I	10.0 v.w.?	10.0 m.	10.2 w.	10.1 m.	10.0 v.w.	10.1 m.
K					7.25 w.	
U			5.7 w.			
U			5.2 w.			
I	4.5 s.	4.5 m.s.	4.5 s.	4.45 s.	4.45 v.s.	4.5 s.
Q	3.33 m.	3.32 s.	3.35 s.	3.35 s.	3.35 s.	3.32 v.s.
I	3.20 m.	3.18 s.				
U					2.92 v.w.	
U	2.62 m.	2.60 s.	2.62 s.	2.60 m.	2.60 s.	2.61 w-m.
I	2.54			2.50 m.	2.56	
Q		2.45 w.				
I	2.42 m.	2.42	2.44 m.			2.43 w.
I					2.27 w.	2.27 v.w.
I	2.17 w.		2.17 w.	2.20 w.	2.17 w.	2.17 w.
I	1.99 v.w.		2.00 w.	2.00 m.	1.99 w.	1.99 v.w.
U					1.92 w.	1.89 v.w.
Q				1.83 w.	1.83 v.w.	1.82 v.w.
Q	1.70 w.	1.70 v.w.	1.68 m.	1.68 w.	1.72 w.	
I	1.66				1.67	1.67 m.
U				1.60 w-m.
Q	1.53 m.s.	1.53 v.w.	1.53 w.	1.53 m.	1.53 m.s.
I	1.50 m.s.		1.50 s.	1.50	1.50 m.s.	
Q			1.38 w.	1.37 v.w.	1.37 w.	
KI			1.29 v.w.	1.29 v.w.	1.29 w-m.	

* See footnote table 22.

TABLE 35
Effect of partial dehydration on interplanar spacings of Hanford colloids

SAMPLE NUMBER	TEMPERATURE	MONTMORILLONITE SPACINGS	KAOLINITE SPACINGS	"X" MINERAL SPACINGS
	°C.	Å.	Å.	Å.
7095	25	15.5	None	10.0
	500	None	10.0
18886	25	None	None	10.1
	100	None	None	10.0
	300	None	None	10.1
	500	None	None	10.0
18887	25	None	7.25	10.0
	100	None	7.25	10.1
	300	None	7.25	10.1
	500	None	None	10.1

TABLE 36a
Interplanar spacings of Madera, Tujunga, and Tule colloids

MINERALS*	MADERA 6528		TUJUNGA 7094		TULE		
	Air-dried	Heated to 500° Å.	Air-dried Å.	Heated to 500° Å.	18890		18891
					Air-dried Å.	Heated to 500° Å.	Air-dried Å.
M	15.0 w-m.	Å.	15.5 s.	Å.	10.0 w.	10.0 w.	15.0 m.s.
IM	10.2 tr.	10.0 m.s.	7.0 v.w.	9.7 w-m.	7.25 m.s.	10.0 w.	9.9 m.
K	7.3 m.	4.5 v.s.	4.5 s.	4.5 s.	4.45 s.	4.5 m.s.	7.3 m.
MI	4.45 v.s.		4.1 w.	4.1 w.	4.20 w.		4.45 v.s.
KI			3.8 w.	3.75 w.			
I					3.52 w.	3.7 v.w.	3.55 m.s.
K							
Q	3.33 m.s.	3.35 s.	3.35 s.	3.35 s.	3.35 s.	3.35 v.s.	{ 3.35 w. 3.20 }
I	3.20 w.	3.20 w.	3.22 s.	3.20 s.			
I	2.97 v.w.	2.98	2.98 w.	2.98 w.			
U	{ 2.64 s. 2.56 }	2.64 s.	{ 2.64 v.s. 2.56 }	2.60 s.	{ 2.62 m.s. 2.52 }	2.62 v.w. 2.52 w.	2.55 s.
MKI							
Q							{ 2.60 m.s. 2.48 }
I	2.44 w.	2.45 w.	2.45 m.	2.43 m.s.			
KIQ							
MKI		2.26 v.w. 2.17 v.w.	2.22 w.			2.45 v.w. 2.30 w.	2.35 w. 2.23 v.w.
I						2.17 v.w.	
K	2.00		2.00 w.		1.97 v.w.		
K			1.83 w.		1.82 v.w.	1.83 w.	
MQ	1.70	1.70 w.	{ 1.70 m.s. 1.66 }	{ 1.70 w. 1.68 }	{ 1.70 m. 1.66 }	1.70 w.	1.70 w.
KIQ	1.66						1.67 m.
KQ	1.53 m.s.	1.53 w.	1.53 s.	{ 1.53 m. 1.50 }	1.53 w-m. 1.50 s.	1.53 w.	1.53 w-m.
MI	1.50 s.		1.50 s.		1.38 w.	1.38 w.	1.50 v.s.
Q					1.29 v.w.		1.29 w.
MKI	1.30 v.w.						1.24 w.
MKI	1.25 v.w.						

* See footnote table 22.

the wide spacings (table 37), leaves some uncertainty as to the clay minerals present, although corresponding data for other colloids have led, in general, to conclusive identification.

As was pointed out earlier in the paper, all these colloids except the Maxwell are chemically similar to the San Joaquin clays, and especially is this true of those tabulated in table 36a. But the x-ray data show that this group of colloids is not characterized by any one type of clay mineral, as is the case

TABLE 36b
Interplanar spacings of Ramona, Placentia, and Maxwell colloids

MIN- ERALS*	RAMONA 7091		PLACENTIA 7092		MAXWELL 17399	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
	Å.	Å.	Å.	Å.	Å.	Å.
M					15.1 v.s.	
IM	10.1 m.	10.1 m.s.		10.1 v.w.		9.8 m.
K	7.3 w.		7.3 w.		7.25 w.	7.3 v.w.
MI	4.45 v.s.	4.5 s.	4.5 s.	4.5 s.	4.5 s.	4.5 s.
I			3.7 v.w.	3.8 m.		
KI			3.6		3.6 w.	3.65 w.
I		3.4 w.	3.4 w.			
Q	3.34 s.	3.33 s.				3.35 w.
I	3.20 w.					3.20 w.
I	2.98 w.	2.93 w.				
U	2.63 m.s.					2.62 s.
MKI	2.56	2.60 v.s.	2.58 s.	2.58 m.	2.60 s.	
Q		2.50 w.		2.50 w.		2.46
I	2.43 m.	2.42 m.	2.40 w.			
Q		2.30 w-m.				
I			2.23 w.	2.25 w.		
I	2.18 w.	2.17 w.		2.17		
KI	2.00 w.	1.99 v.s.	2.00 w.			
M						1.72 v.w.
MQ	1.70 w.	1.70 w.	1.70 s.		1.68 w.	
KIQ	1.66	1.66	1.66			
KQ	1.53 m.s.	1.53 v.s.	1.53 w.	1.53 m.	1.53 w.	1.54 m.s.
IM	1.50 m.s.		1.50 s.		1.50 m.	1.50 w-m.
Q		1.37 w.				
MKI		1.32 w.			1.30 w.	1.30 w.

* See footnote table 22.

with most of those previously discussed in this paper. Excluding the Maxwell, which is of a different type, the other six samples show great diversity in their clay mineral content. Three show montmorillonite spacings, all but one show kaolinite spacings, and three show spacings associated with the "x" mineral. Only the Ramona and Placentia soils were found to contain clay minerals similar to those of the San Joaquin series.

The Madera pattern for the unheated material shows a definite but weak

montmorillonitic 15Å. spacing (table 36a). It is not surprising that a corresponding 9.5Å. spacing was not observed in the pattern for the heated material, as the reflection would necessarily be very diffuse and more or less merged with that of the near-by 10Å. spacing of the "x" mineral which the pattern contains.

In the high-temperature patterns for the Tujunga and the lower horizon of the Tule (sample 18891), the 9.7 and 9.9 spacings respectively, are taken to indicate the contracted montmorillonite spacing rather than the 10Å., the "x" mineral spacing, since with the low-temperature samples the 15Å. spacing was strong in both and the 10Å spacing was absent.

TABLE 37
Effect of partial dehydration on the interplanar spacings of various colloids

SERIES	SAMPLE NUMBER	TEMPERATURE	MONTMORILLONITE SPACINGS	KAOLINITE SPACINGS	"X" MINERAL SPACINGS
		°C.	Å.	Å.	Å.
Madera	6528	25	15.0	None	10.2
		500	None	None	10.0
Tujunga	7094	25	15.5	7.0	None
		500	9.7	None	None
Tule	18890	25	None	7.25	None
		500	None	None	None
Tule	18891	25	15.0	7.3	None
		500	9.9	None	None
Ramona	7091	25	None	7.3	10.1
		500	None	None	10.1
Placentia	7092	25	None	7.3	None
		500	None	None	10.1
Maxwell	17399	25	15.1	7.25	None
		500	9.8	7.3	None

It will be noted that the montmorillonite spacing is shown in the lower (sample 18891) but not in the upper horizon (sample 18890) of the Tule soil.

On the basis of the x-ray data in table 37, the Maxwell clay appears to contain both montmorillonite and kaolinite or similar clay minerals. In view of the origin of this material, however, the persistence of the 7Å. spacing in the heated material does not necessarily indicate kaolinite. The 7Å. line as well as other lines in the kaolinite pattern have been observed by the authors to persist even after heating to 500° for a considerable period, but it has been further observed that all kaolinite lines disappear completely if the heating to 500° has been sufficiently prolonged. Where kaolinite lines persist after

the wide spacings (table 37), leaves some uncertainty as to the clay minerals present, although corresponding data for other colloids have led, in general, to conclusive identification.

As was pointed out earlier in the paper, all these colloids except the Maxwell are chemically similar to the San Joaquin clays, and especially is this true of those tabulated in table 36a. But the x-ray data show that this group of colloids is not characterized by any one type of clay mineral, as is the case

TABLE 36b
Interplanar spacings of Ramona, Placentia, and Maxwell colloids

MIN- ERALS*	RAMONA 7091		PLACENTIA 7092		MAXWELL 17399	
	Air-dried	Heated to 500°	Air-dried	Heated to 500°	Air-dried	Heated to 500°
	Å.	Å.	Å.	Å.	Å.	Å.
M					15.1 v.s.	
IM	10.1 m.	10.1 m.s.		10.1 v.w.		9.8 m.
K	7.3 w.		7.3 w.		7.25 w.	7.3 v.w.
MI	4.45 v.s.	4.5 s.	4.5 s.	4.5 s.	4.5 s.	4.5 s.
I			3.7 v.w.	3.8 m.		
KI			3.6		3.6 w.	3.65 w.
I		3.4 w.	3.4 w.			
Q	3.34 s.	3.33 s.				3.35 w.
I	3.20 w.					3.20 w.
I	2.98 w.	2.93 w.				
U	2.63 m.s.					2.62 s.
MKI	2.56	2.60 v.s.	2.58 s.	2.58 m.	2.60 s.	
Q		2.50 w.		2.50 w.		2.46
I	2.43 m.	2.42 m.	2.40 w.			
Q		2.30 w-m.				
I			2.23 w.	2.25 w.		
I	2.18 w.	2.17 w.		2.17		
KI	2.00 w.	1.99 v.s.	2.00 w.			
M						1.72 v.w.
MQ	1.70 w.	1.70 w.	1.70 s.		1.68 w.	
KIQ	1.66	1.66	1.66			
KQ	1.53 m.s.	1.53 v.s.	1.53 w.	1.53 m.	1.53 w.	1.54 m.s.
IM	1.50 m.s.		1.50 s.		1.50 m.	1.50 w-m.
Q		1.37 w.				
MKI		1.32 w.			1.30 w.	1.30 w.

* See footnote table 22.

with most of those previously discussed in this paper. Excluding the Maxwell, which is of a different type, the other six samples show great diversity in their clay mineral content. Three show montmorillonite spacings, all but one show kaolinite spacings, and three show spacings associated with the "x" mineral. Only the Ramona and Placentia soils were found to contain clay minerals similar to those of the San Joaquin series.

The Madera pattern for the unheated material shows a definite but weak

montmorillonitic 15Å. spacing (table 36a). It is not surprising that a corresponding 9.5Å. spacing was not observed in the pattern for the heated material, as the reflection would necessarily be very diffuse and more or less merged with that of the near-by 10Å. spacing of the "x" mineral which the pattern contains.

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TABLE 37
Effect of partial dehydration on the interplanar spacings of various colloids

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		°C.	Å.	Å.	Å.
Madera	6528	25	15.0	None	10.2
		500	None	None	10.0
Tujunga	7094	25	15.5	7.0	None
		500	9.7	None	None
Tule	18890	25	None	7.25	None
		500	None	None	None
Tule	18891	25	15.0	7.3	None
		500	9.9	None	None
Ramona	7091	25	None	7.3	10.1
		500	None	None	10.1
Placentia	7092	25	None	7.3	None
		500	None	None	10.1
Maxwell	17399	25	15.1	7.25	None
		500	9.8	7.3	None

It will be noted that the montmorillonite spacing is shown in the lower (sample 18891) but not in the upper horizon (sample 18890) of the Tule soil.

On the basis of the x-ray data in table 37, the Maxwell clay appears to contain both montmorillonite and kaolinite or similar clay minerals. In view of the origin of this material, however, the persistence of the 7Å. spacing in the heated material does not necessarily indicate kaolinite. The 7Å. line as well as other lines in the kaolinite pattern have been observed by the authors to persist even after heating to 500° for a considerable period, but it has been further observed that all kaolinite lines disappear completely if the heating to 500° has been sufficiently prolonged. Where kaolinite lines persist after

heating, a perceptible diminution in intensity is usual. In the present instance, the line representing the 7\AA . spacing is weak in both the heated and the unheated material. Since the Maxwell soil is known to have originated from the weathering of serpentine rocks, it is pertinent to inquire whether the 7\AA . spacing might be due to finely divided residues from serpentine minerals. It is known, for example, that chrysotile, a mineral in the serpentine class, contains a spacing of 7.32\AA . which, on the basis of cell dimension data by Bragg (4), has Miller indexes (200). We intend to investigate more fully the possible presence of serpentine residues in the colloidal clay minerals.

The data in tables 36a and 36b show strong reflections due to quartz spacings in four of the seven colloids, but with the three remaining colloids, the indications of quartz were much less definite. These colloids are almost entirely free from spacings other than those of the clay minerals and quartz.

DISCUSSION

It is worthy of note that the colloids of a high percentage of the soils studied in this investigation were found to be decidedly heterogeneous. This heterogeneity involves both the kind of clays and the minor amounts of other classes of minerals which they contain. Although the colloid of every soil examined was composed chiefly of clay minerals, more than one type of clay mineral was usually present in a given sample. With but few exceptions, however, the colloid of each soil appears to be dominated by a single type of clay, but it should be emphasized that too few soil profiles were included in this study to warrant definite conclusions as to the specific type of clay that is characteristic of given soil series. The results indicate that in the Yolo series montmorillonitic clays predominate; in the Redding, Sierra, Vina, Keefers and Tule series, kaolinitic clays appear to predominate; and in the San Joaquin and Hanford soils the clay is more largely of the muscovitelike type, referred to herein as "x" mineral.

It should be emphasized that the word "montmorillonite," as used in this paper, refers not to the specific mineral, montmorillonite, but rather to the group to which this mineral belongs. This group includes montmorillonite, beidellite, nontronite, and probably saponite, all of which appear to be characterized by the shifting position of one of their diffraction lines, depending on the water content of the sample. We have merely made use of this property for the purpose of identification.

The kaolinitic clays, as used herein, include both kaolinite and halloysite. It is possible that halloysite was the chief member of this group in the soils studied. Mehmel (30) showed that halloysite loses water at 50°C ., passing into metahalloysite, which is very similar structurally to kaolinite. Hendricks (16) has recently shown that hydrated halloysite loses water, apparently irreversibly, upon standing in the laboratory. He suggested that the ordinary form of halloysite is probably identical with Mehmel's metahalloysite. Since the soils reported in this paper were taken from comparatively dry and hot

climates, any halloysite that they contain was probably the partially dehydrated form, which is difficult to distinguish from kaolinite.

With a large percentage of these colloids, base-exchange capacity was found to be roughly proportional to $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio, which agrees with previously published results of other investigations. This correlation, however, was far from perfect, and a few marked exceptions were found. For example, samples 18889, a San Joaquin clay, and 16054, a Vina sample, have the same $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio, but their base-exchange capacities differ more than 50 per cent (40 vs. 61.7); and colloid 6530, another San Joaquin sample, with a $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio of 3.20, has a base-exchange capacity of only 27.6, whereas 16055, a Vina sample, has a ratio of 2.94, and yet its capacity was 64, which is one of the highest found in the entire list of 44 colloids investigated. Since the samples were distinctly heterogeneous in mineral composition, a close correlation between the $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio and base exchange is not to be expected. Quartz, in minor and probably variable amounts, was present in all the samples; moreover, the other nonclay minerals, together with any amorphous SiO_2 that was present, would certainly exert some influence on the $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio and thus tend to upset the correlation with base-exchange capacity. Moreover, the distribution of particle sizes may have differed substantially in the different samples, and this might affect base-exchange capacity to some extent.

The ratio of SiO_2 to R_2O_3 is influenced by a factor additional to those already mentioned, namely, uncombined Fe_2O_3 . Analysis of the buffered acid extracts obtained in the treatment of the samples for the special optical studies reported in table 19, showed that 50 or more per cent of the total iron is uncombined in these colloids. The color of the samples before acid treatment was red, after treatment, gray. In view of these facts, it is obvious that the $\text{SiO}_2\text{-R}_2\text{O}_3$ ratio can give but the merest suggestion as to the specific minerals present. Of course, with strongly lateritic colloids, such as the Nipe (8), this ratio indicates that much of the sesquioxide is present in nonsilicate form. The mere presence of uncombined Fe_2O_3 , however, is hardly a useful criterion of laterization, since uncombined Fe_2O_3 is probably present in variable amounts in most soil colloids.

There appears to be no definite relation between content of nonreplaceable forms of the ordinary bases and base-exchange capacity or other properties of these colloids. It is true, the montmorillonitic types tended to be relatively high in Mg, the Yolo and Maxwell clay colloids being the highest in total Mg found. However, the colloid of the B horizons of the Palermo Redding samples, although predominantly montmorillonitic and high in base-exchange capacity, contain much less Mg than the Yolo and Maxwell clays. Moreover, the Ramona, Placentia, Tujunga, and Madera clays are not predominantly montmorillonitic, nevertheless they contain more Mg than the Palermo Redding colloids. As is well known, the bentonitic clays usually contain Mg, but as will be shown in another paper, their base-exchange properties are not

proportional to Mg content. It seems doubtful whether Mg plays any important part in the base-exchange properties of these colloids.

Neither is the content of K a significant index to the properties of these colloids. Those which contain the highest proportions of mineral "x" tended to be relatively high in K, but the same is also true of Yolo samples 431 and 7083, neither of which contains significant amounts of mineral "x." It is likely that K was present in these colloids, in part at least, as a constituent of accessory minerals other than the true clays. The mineral "x" may possibly contain K as an essential constituent.

Moreover, K content of these colloids is not directly proportional to the maturity of the profile. For example, the Davis Yolo clays, although obtained from a soil which shows very feeble profile development, contain less K than the colloid of the Keefers, which is a highly weathered and mature soil. This, of course, need not occasion surprise, since the parent material of the Davis Yolo soil is composed of comparatively recent alluvium, some, at least, of which may have been eroded from areas that had already undergone extensive weathering and leaching before being transported to the Davis area. It is probable that, among soils of common origin and similar geological history, the content of K and Na will bear some direct relation to intensity of leaching, but the soils studied in this investigation do not meet this requirement. As has been pointed out, the Ca content of these colloids was mainly determined by their base-exchange capacity, but the amounts of Ca found afford but little clue to pedological processes, since the samples were artificially saturated with Ca. The ratio of bases to SiO_2 or sesquioxide in these colloids is, therefore, of doubtful significance.

Particular attention has been paid to the Vina samples, in view of the fact that their base-exchange capacity is relatively high, despite their kaolinitic nature. A sample was separated into two fractions, namely, particles from $1.0\text{--}0.25\ \mu$ in diameter, and those less than $0.25\ \mu$, but no material difference was found in their chemical composition, base-exchange capacity, or x-ray properties. The same x-ray lines were produced by each, and those of the coarser ($0.25\text{--}1.0\ \mu$) fraction were no more distinct than those of the finer fraction. The conclusion seems reasonable, therefore, that the faintness of the x-ray lines produced by this type of colloid was probably not due to its being composed of exceptionally small sized particles. It is more probable that this colloid is less well crystallized than most of the other types studied.

As shown in the section on x-ray investigation, two of the samples of Vina colloid gave some evidence of montmorillonitic clay, in addition to the much greater amount of the kaolinitic type. The relative proportions of the two types of clay cannot now be estimated. We can only say that the kaolinitic lines were much stronger than those of the montmorillonitic lines, and that the latter were much weaker than those of the Yolo clays, which are clearly predominantly montmorillonitic.

The fact that the two fractions of the Vina clay, referred to above, have almost identical base-exchange capacity and chemical composition is in har-

mony with the recent results of Hauser and Reed (15) on Wyoming bentonite; but they disagree with the results which Marshall (29) obtained with one bentonite and two soil colloids, those of Whitt and Baver (37) on Putnam Clay, and also those of Bray (7) on colloids from Illinois.

Among the colloids investigated, there appears to be no dependable correlation between kind of clay mineral and base-exchange capacity. It is true, the montmorillonitic types all have relatively high base-exchange capacity, whereas certain kaolinitic types have low base-exchange power. But the Vina samples, one of which appears to contain no clay mineral except the kaolinitic type and the other two of which are predominantly kaolinitic, all have about as high base-exchange capacity as the montmorillonitic types. Moreover, certain of the more purely kaolinitic types, the Keefers, for example, have comparatively high base-exchange capacity, and the Hanford and San Joaquin samples gave still higher figures for base-exchange capacity, yet their clays are predominantly of the muscovitelike type and, for the most part, virtually free from montmorillonitic clay.

These results are difficult to harmonize with the idea that, apart from organic matter, base exchange in soils is due either to a single chemical substance or to one type of clay mineral. The results also bear on the question as to the position of the exchangeable ions on the lattice, but this question will not be discussed here.

The reference to the size of the grains and flakes, observed in the optical studies, should not be confused with the previous statement that the upper limit of particle size was approximately $1\ \mu$. These comparatively large grains and flakes were composed of many small particles which coalesced and partially oriented during the processes of Ca saturation and drying. Proof of particle size was obtained by direct microscopic observation on an aqueous suspension of Na-saturated samples of several different colloids. It was found that a 0.1 per cent suspension of the Na-saturated form was, in every case, composed of particles $1\ \mu$ or less in diameter. As is well known, Na-saturated colloids are usually much more completely dispersed than the Ca form. Gedroiz (11) showed, for example, that Na saturation of certain Russian soils substantially increased the clay content as found by mechanical analysis.

This investigation shows that it is possible to arrive at a fairly definite understanding of soil colloids by using a combination of methods of study. The four independent methods used in this work; namely, chemical analysis, dehydration, optical, and x-ray investigation, usually gave consistent results. The indications afforded by this work are that a thorough study of the colloid, not only will throw important light on the general properties of the soil, but may also be utilized as a material aid in soil classification.

It is especially interesting that in certain profiles of the Redding and also the Tule series, the relative content of montmorillonitic clay tends to increase with depth. The same tendency has recently been found in a Susquehanna profile (25).

In view of the wide differences in the clay mineral content of the colloids

of the different soil types, which in turn probably caused variations in base-exchange capacity, the thermal loss of water, particularly at 100°C., and probably differences in swelling upon wetting and contraction upon drying, it is hardly likely that the water regimes and crop responses of different soils will be definitely correlated with total clay content. It is virtually certain that the surface soil of Yolo loam, for example, has properties significantly different from those of Sierra or Redding loam. In this connection, it is important to remember that, in all probability, the variable nature of the noncolloidal constituents which are known to occur in soils also exerts important influences. These constituents, together with the variable physical nature of the profile of different soil types, all influence crop production.

SUMMARY

The colloids of the Yolo and the San Joaquin family of soils (San Joaquin, Ramona, Placentia, Hanford, and Tujunga) were found to contain substantial amounts of nonexchangeable Mg, and the Maxwell clay is exceptionally high in Mg. Base-exchange capacity, however, is not proportional to Mg content. For example, two of the Vina clays are low in Mg but high in base-exchange capacity. Nonexchangeable Na was low in every sample investigated, and K also was comparatively low. The San Joaquin clays and certain of the Hanford and Yolo samples were the highest in K found.

The $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio of the Yolo and of certain samples of the San Joaquin series was approximately 4, whereas that of the Sierra, Keefers, and certain Redding profiles approached 2. This ratio in most of the other samples lies between 2 and 4. In the Maxwell it was found to be almost 5. Although there is a rough proportionality between $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio and base-exchange capacity, the correlation is not high, and in certain cases it appears to be negative.

The dehydration curves appear to be somewhat characteristic of each type of colloid, the shape of the curve depending very largely on the kinds and relative proportions of the different clay minerals present. The dehydration curves of the Yolo and Maxwell clays resemble those of the bentonitic clays, and the curves for the Sierra, Keefers, and certain Redding samples are similar to the curves for kaolinite and halloysite. A relatively good correlation was found between water loss at 100°C. and 150°C., respectively, and base-exchange capacity.

Their optical properties show that these colloids are preponderantly crystalline. The birefringence (γ minus α) was approximately .020 in the Yolo and in the B₂ horizon of the Redding from Palermo. The birefringence of the Tujunga, Hanford, Ramona, Placentia, San Joaquin, and Madera clays was also comparatively high. Those colloids with low $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios also have low birefringence. Quartz was found in every sample, and rutile and zircon were tentatively identified in several samples.

Saturation with Ca, Mg, K, or Na appears to have but little influence on the optical properties of these colloids.

In the air-dried condition the ultimate particles of these colloids arrange themselves in the form of comparatively large flakes or grains, which appear to act as single optical units in all respects except one, namely, these flakes were crowded with minute inclusions which have optical properties altogether different from those of the flakes as a whole. In aqueous suspension these flakes tend to break down. The Na-saturated form, when studied in a dilute suspension, showed scarcely any large flakes. Instead, all visible particles were approximately $1\ \mu$ or less in diameter.

Removal of the more soluble and probably uncombined Fe_2O_3 lowered the indexes of refraction in all samples studied.

X-ray analysis showed that every colloid studied is definitely crystalline and composed chiefly of clay minerals of different types. The Yolo and Maxwell clay colloids are predominantly montmorillonitic; the Sierra, Redding, Vina, and Keefers colloids are preponderantly kaolinitic; and the San Joaquin and Hanford colloids are largely composed of the "x" clay mineral, similar to illite. Certain samples from different soil types were found to be composed of mixtures of these clay minerals.

The optical properties, while less diagnostic, are consistent with the conclusions from x-ray study. It is thought that the high indexes of refraction are due to admixed iron oxide, and that the occasional high double refraction found, for example, in certain Redding clays, may indicate "form double refraction."

In addition to the clay minerals, x-ray investigations showed that quartz was also present in minor amounts in every sample, and rutile and zircon were probably present in certain samples.

It is possible to determine the types of clay minerals present in soil colloids by comparing the x-ray diffraction patterns with those of known minerals. The determination is especially facilitated by x-raying the samples at widely varying moisture content. The dehydration curves of the different clay minerals show that OH lattice constituents pass off as water vapor at temperatures which are characteristic for each class. The consequence is their x-ray diffraction pattern is destroyed at these temperatures.

One of the most characteristic x-ray lines of the montmorillonitic clays corresponds to a spacing of about 15\AA . in the air-dried form of the clay and of from 9.5 to 10\AA . in the material heated to 500°C . The diffraction line characteristic for the identification of the kaolinitic clays corresponds to a spacing of about 7.0\AA .; this spacing is not affected by heat treatment below the temperature of decomposition, but at about 500°C . this, as well as the other lines of these clays, disappears as a result of decomposition. The corresponding line of the "x" mineral is found at about 10\AA . and remains in this position until the sample is heated above 500°C . By combination of partial dehydration with x-ray analysis, therefore, it is possible to determine what clay mineral is present, whether alone or as mixtures of other types of clays. If crystalline minerals other than the clays are present, their identity can, in some cases at least, be established by reference to the diffraction patterns of known minerals.

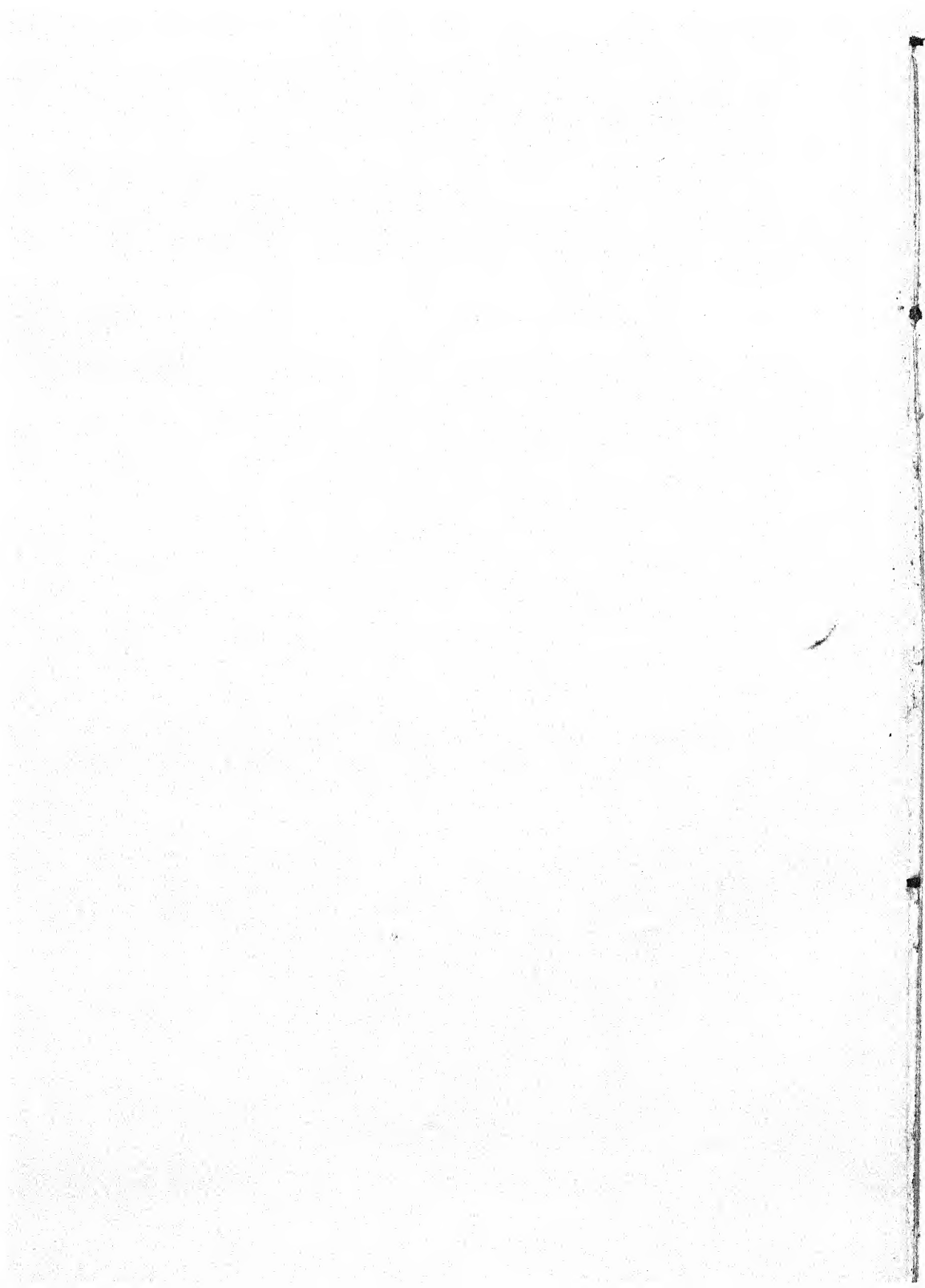
While x-ray analysis affords a means of identification of the several classes of minerals present in soil colloids, it does not necessarily yield all the important information about soil colloids. A combination of two or more types of methods is the more instructive.

In view of the fact that many California soil types were not included in this work, and that an inadequate number of samples of several of the types used were studied, the conclusions drawn in this paper should be regarded as tentative. Much further work will be required for a full elucidation of this subject.

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MINERALS PRESENT IN SOIL COLLOIDS: I. DESCRIPTIONS AND METHODS FOR IDENTIFICATION

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The clay fraction of soils has long been recognized as playing an important part in determining the properties of soils. Early methods for studying this fraction were chiefly restricted to chemical analyses because the small particle size did not permit application of mineralogical technics then available. Chemical analyses showed that the principal constituents of the colloids are oxygen, silicon, aluminum, and iron, with lesser amounts of magnesium, potassium, sodium, calcium, and titanium. But the manner of combination of these constituents could not be determined from the chemical composition, and analytical methods now are recognized as giving only partial information on the question of mineral composition.

It was not until the application of x-ray diffraction that the essential crystallinity of the colloidal fraction of soils was fully demonstrated, although a few mineralogists had recognized the fact, and possible combinations of the constituents were determined. This development was made possible by the rapid advance in knowledge of the structures and ranges of compositions of the clay minerals. Applications of methods now available make possible identification of the major inorganic components of soil colloids and semiquantitative estimation of their amounts.

Although much work has been done on the mineralogy of the clays, the nomenclature of some of the groups is still confused and there is doubt about some of the details of crystal structures. It is a purpose of this article to attempt a presentation of the subject suited to the needs of the soil scientist. Methods adequate for identification of the mineral constituents of soil colloids also are described in this paper and will be illustrated by application to a group of soil colloids in the following paper.

THE CLAY MINERALS

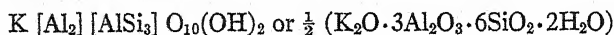
Though the older literature on clays is extensive, the major progress has been made in the last decade. Several articles reviewing recent work have appeared (8, 19, 21, 24, 25, 26, 29), and considerable analytical data have been summarized by Von Engelhardt (8). Much of the extensive work of Dr. C.

¹ Bureau of Chemistry and Soils.

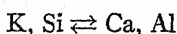
² Bureau of Plant Industry.

S. Ross, of the U. S. Geological Survey, has not yet been published, however, and a number of crystal structure determinations of clay minerals made in the U. S. Bureau of Chemistry and Soils have not appeared. The following summary depends in part upon this unpublished work and upon many discussions with others.

Classification of clay minerals necessarily depends upon their crystal structures, but it is perhaps best to direct attention first to changes in their chemical compositions as affected by substitution of one element for another, that is, by isomorphous replacements. Such changes are well illustrated by the micas, in which they are very extensive. Although these were known to early mineralogists, it was only after the x-ray investigations of Maugin (27) that the kind and extent of the replacements were fully realized. The ideal³ composition of muscovite can be expressed as



the brackets enclosing groups of atoms which occupy similar positions in the crystal lattice. Isomorphous replacements in muscovite as well as other minerals are determined more by the relative sizes of the various ions than by their chemical similarities. Thus potassium in muscovite can be replaced to a limited extent by the somewhat smaller sodium ion but not by the much smaller lithium ion. Aluminum, enclosed in the first bracket, is surrounded by six oxygen and hydroxyl ions at the corners of an octahedron. It can be replaced by Ti^{+2} , Fe^{+3} , Fe^{+2} , Mg^{+2} , Mn^{+2} , Mn^{+3} and Li^{+3} , which are similar to it in size. Electrical neutrality is maintained by accompanying changes, thus $[Al_2^{+3}]$ can be replaced by $[Mg_2^{+2}]$, leading to mica phlogopite. Silicon in the second bracket has tetrahedral coordination and can only be replaced by aluminum. There can be simultaneous replacements of the type



the Ca, Al mineral being the brittle mica, margarite. Finally, hydroxyl can be replaced by fluorine, and oxygen can sometimes be substituted by hydroxyl. These replacements must be given careful consideration since they depart greatly from chemical expectations and seriously affect the manner in which oxide ratios such as $R_2O_3:SiO_2$ should be regarded.

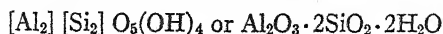
The clay minerals which are common constituents of soil colloids can be divided into three general groups: (a) kaolin minerals, (b) montmorillonites, and (c) hydrous micas. These will be discussed in the order given.

The kaolin minerals

The mineralogy and compositions of the kaolin minerals have been extensively studied by Ross and Kerr (32, 33), who have discussed the various

³ The term "ideal" is used for the chemical formula that serves as a basis for discussion of isomorphous replacements. It is usually called "the end member of a series" by mineralogists and represents an approach to the composition associated with the mineral name.

names that have been used. The ideal composition is



and there are four polymorphic varieties: (a) kaolinite, (b) nacrite, (c) dickite, and (d) halloysite. Isomorphous replacement in these minerals is largely restricted to mutual substitutions of Al and Si in the $[\text{Si}_2]$ positions, with resulting variation in $\text{SiO}_2:\text{R}_2\text{O}_3$ ratio from 1.6 to 2.9:1, as shown by Ross and Kerr. Ratios below 2.0 are a result of replacement of Si by Al with accompanying changes in $[\text{Al}_2]$ positions or substitutions of oxygen by hydroxyl. It is not known on the basis of structure how ratios greater than 2.0 come about, and kaolinites with such ratios are usually called "anauxite." Particular attention is directed to the fact that kaolin minerals do not contain appreciable iron or magnesium, neither of these exceeding one mol per cent.

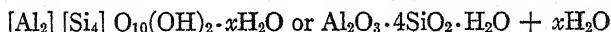
Only kaolinite and halloysite have been reported as occurring in soils, nacrite and dickite being of hydrothermal origin. Another mineral related to the kaolins is hydrated halloysite, the composition of which can be represented as



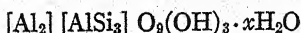
This mineral easily loses two molecules of water by air drying from the above formula, changing to halloysite which has not been rehydrated in the laboratory. It has not been observed as a constituent of soils.

Montmorillonites

Analyses of montmorillonites are listed by Von Engelhardt (8), Hofmann and Bilke (16), and Nagelschmidt (28). A more extensive collection together with mineralogical characteristics and a discussion of nomenclature will soon be published by Dr. C. S. Ross. The ideal formula is



and the same types of isomorphous replacements as outlined for mica take place. Substitution of $[\text{Al}_2]$ by $[\text{Mg}_3]$ gives the formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + x\text{H}_2\text{O}$, which is that of the mineral magnesium bentonite (9). The name "bentonite" is often used as synonymous with "montmorillonite," but more strictly it refers only to material derived from volcanic ash and might sometimes be related to the micas rather than to the montmorillonites; that is, bentonite is a rock rather than a mineral name. Analyses have been published in which the amount of SiO_2 exceeds that required by the above formulas, but this condition probably always results from the presence of silica as an impurity, as has been definitely proved for a number of samples. Substitution of $[\text{Al}_2]$ by $[\text{Fe}_2]$ leads to the mineral nontronite with the ideal formula $\text{Fe}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, the Fe being predominantly ferric. In any of these minerals, silicon in tetrahedral coordination can be replaced by aluminum, and the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio (the Al_2O_3 including the isomorphous replacement) can approach 2:1, a possible formula being



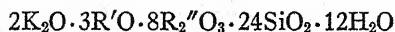
or, instead of oxygen's being replaced by (OH), further ions can be substituted with octahedral coordination; that is, in the $[Al_2]$ positions. These minerals are usually called "beidellite," the $SiO_2:(R_2O_3 + RO)$ ratio in many instances being near 3:1.

The structure studies of Hofmann and his associates (16, 17, 23) have shown the manner in which montmorillonites reversibly take up water between the aluminosilicate layers of the lattice. This water is represented by xH_2O , being indefinite in amount, in the above formulas and accounts for the swelling properties of the minerals. Montmorillonites are further of interest in that they show greater base exchange capacity than do the other clay minerals. The calcium, the amount of which usually is much less than that of magnesium in montmorillonites, apparently is present as exchangeable ions which are external to the lattice and should not be considered an essential part of the formula.

Hydrous micas

At present it is debatable what name should be given to the clay minerals related to the micas. These minerals were first recognized as components of soil colloids by Hendricks and Fry (15) under the name "ordovician bentonites," a term that had been used by Ross and Shannon (34). They have now been investigated very thoroughly by Grim, Bray, and Bradley (10) and by Hofmann and his co-workers (7, 18). The former group of authors used the name "illite"; and the latter, "glimmerton" or the "micalike mineral" of the clays. Other names that have been used include "bravistite," and "hydromica" (7, 10, 18). Glauconite is probably a related mineral.

The ideal formula can be considered to be the same as that given for mica, but the minerals always contain less potassium and more water. Grim, Bray, and Bradley give the formula



as representing the average of their analyses of illite. The composition is obtained from the ideal mica formula



by replacement of K by H_2O accompanied by substitution of Si for Al in tetrahedral coordination, or (OH) for O to keep the charge balanced. These minerals contain appreciable Mg and Fe (both ferric and ferrous) replacing $[Al_2]$ with octahedral coordination and thus are more closely related to biotite than to muscovite. The amount of K_2O is very variable, the total range being from the order of 1 per cent to that required for muscovite (11.8 per cent K_2O). Many of the analyzed samples, however, contain almost 5 per cent K_2O , which can be taken as an average value.

Glauconite, the essential component of greensands, is perhaps the mineral of this type that has been recognized for the longest time. Both its iron

and potassium contents are greater than those of the material described as illite, and its water content is less. Glauconite thus more closely approaches the mica biotite in composition, and its close structural similarity to biotite has been demonstrated (13).

Particular attention is directed to the work of Denison, Fry, and Gile (5) on the alteration of muscovite and biotite in the soil. These investigators followed changes in composition of the coarse-grained micas undergoing weathering. Their many analyses of samples selected with mineralogical control show continuous variations from the pure micas through the glauconite and illite ranges. The weathering of mica in the soil is accompanied not only by decrease in potassium and increase in water content but also by decrease in iron and magnesium with accompanying increase in aluminum.

Perhaps it is evident from this discussion that the gradation in composition is so continuous as hardly to justify the naming of intermediate minerals. For this reason the entire series will simply be referred to as "hydrous micas," since this name shows their relationship to the micas while indicating the nature of departure. "Hydromica" can not be used as a name, since it has been used in other ways in mineralogical literature.

Kaolins, montmorillonites, and hydrous micas, as well as micas, brittle micas, chlorites, brucite, vermiculite, talc, and a number of other minerals⁴ that do not occur in soil colloids have closely similar structures, as was first shown by Pauling (31). They all contain alumino-silicate layers (with isomorphous replacements) between which there is perfect cleavage, and individual crystals contain many superimposed layers. Gruner (12) has shown that minerals can be formed by interstratification of different kinds of layers. He gave the name "hydrobiotite" to such a composite of vermiculite and biotite, the composition being similar to that of hydrous micas. This type of mixed mineral is difficult to recognize, but it is probably a common constituent of soils. In particular, montmorillonites and hydrous micas probably occur together in a manner similar to Gruner's hydrobiotite. In fact, it is somewhat questionable that individual montmorillonite crystals are common constituents of soils although they undoubtedly are present in some.

Accessory minerals of soil colloids

Free oxides and free hydrous oxides of iron are common constituents of soils, to which they impart red or yellow color. The common minerals present are hematite, Fe_2O_3 , and goethite, $\text{FeO}(\text{OH})$. Goethite is often called "limonite," a name that includes not only goethite but also amorphous material approximating $\text{FeO}(\text{OH})$ in composition as well as lepidocrocite, which has not been identified in soils.

There has been some discussion as to the state of combination of the titanium which is always present in soil colloids in amounts of the order of 0.5 per cent or greater. It frequently has been suggested that the titanium is chiefly in

⁴ See Bragg (3, p. 203-229) for a clear discussion of the structure of these minerals.

combination with the silicates, replacing aluminum (35). Though some of it is undoubtedly in this form, it is probable that separate titanium-bearing minerals are present, particularly leucoxene, the composition of which is indefinite. Alteration of titanium minerals such as ilmenite to leucoxene has been observed microscopically in coarse fractions of unconsolidated materials.

It is probable that other minerals are occasional constituents of soil colloids. Among these are the oxides of aluminum such as the minerals diaspore, $\text{AlO}(\text{OH})$, böhmite, $\text{AlO}(\text{OH})$, and Gibbsite or hydrargillite $\text{Al}(\text{OH})_3$, which are components of bauxite. Quartz (SiO_2) is probably always present, but its amount depends strongly on the upper particle size limit chosen in separating the soil colloid. It is possible, too, that amorphous silica might sometimes be present as a minor constituent. Calcium carbonate in the form of calcite is sometimes present, as also are phosphorus-bearing minerals.

METHODS FOR IDENTIFYING AND ESTIMATING COMPONENTS OF SOIL COLLOIDS

Chemical methods

It is evident from the foregoing discussion that the $\text{SiO}_2:\text{R}_2\text{O}_3$ ratio of the soil colloid must be used with extreme caution for identification of the component minerals since they overlap in this ratio and since some of the oxides, particularly those of iron, may or may not be combined with silica, and silica may be free. If analyses are made after removal of free oxides of iron and it is borne in mind that aluminum can be replaced by magnesium, and iron, then the hydrous micas and montmorillonites generally have a higher $\text{SiO}_2:(\text{R}_2\text{O}_3 + \text{RO})$ ratio than kaolinite or halloysite, as well as a higher $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio. Since most colloids are mixtures of these minerals, however, no great use can be made of such ratios for identifying the mineral components.

Free oxides of iron in a soil colloid can be readily removed and determined by the use of nascent H_2S according to the method of Truog and his associates (36). If the amount of iron combined with silica as found in this manner exceeds 2 per cent Fe_2O_3 , hydrous micas, montmorillonites, or their mixed layer minerals are present. Absence of combined iron does not indicate, however, that these minerals are absent, as is evident from the discussion of their compositions.

Determination of nonexchangeable potassium gives information on the presence of hydrous mica, as potassium is an essential constituent only of this mineral among the common minerals of the soil colloid. It has already been pointed out that the potassium content of hydrous micas is variable and this limits the use of the analytical data for quantitative estimation. Colloids containing more than 1 per cent of nonexchangeable potassium, as examined to the present time, have hydrous micas as a prominent constituent.

Magnesium can be extensively substituted for aluminum in the clay minerals other than those of the kaolinite group, and such minerals are present when the amount of nonexchangeable magnesium in the colloid is appreciable, exceeding about 1 per cent. Thus determination of magnesium gives the same type of information as does determination of iron combined other than

as oxides. It is best, however, to know both, since one or the other replacement might predominate. It further should be emphasized that calcium does not replace magnesium in the clay minerals and when present other than as carbonate, sulfate, or phosphate, is exchangeable.

X-ray diffraction methods

X-ray studies have been most useful in showing that the colloidal fraction of soils predominantly contains crystalline clay minerals and in determining the structure of these minerals. Observations on soil colloids are restricted to powder diffraction patterns which are used in a strictly empirical manner by comparison with known minerals. Isomorphous replacements such as those found in the clay minerals affect the patterns only slightly, the greatest effect being produced on intensities by substitution of iron for aluminum.

TABLE 1

Characteristics of reflections from the cleavage planes of clay minerals occurring in soil colloids

MINERAL	KAOLINITE	HYDROUS MICA	MONTMORILLONITE, AIR-DRIED (19)
Spacing of (00n)	7.1	10.0	15.0
Intensity of n*	s†	ms	vs
2 n	vs	m	m
3 n	w	vs	a
4 n	w	w	a
5 n	vw	s	s
6 n		vw	a

* Intensities are for Cu K α radiation in cylindrical camera of type shown in plate 1.

† The following abbreviations are used: n, the order of the spectrum; s, strong; m, medium (ms); w, weak; a, absent; v, very (vw, vs).

Ordinary powder diffraction data for the clay minerals have been given in several places (14), suitable references being for kaolinite (11, 15), hydrous mica (7, 10, 15), and montmorillonite (15, 17). Since the clay minerals have many structural elements in common, this type of data is not the best for differentiating them. Their most characteristic differences are in their interplanar spacings normal to the plane of perfect cleavage [(001) in crystallographic nomenclature].

Clay minerals, being micaceous in habit, separate from suspensions with many of the individual plates approximately parallel to the surface on which they settle. The spacings of (001) can best be obtained from such oriented samples, and the type of camera described by Clark, Grim, and Bradley (4), which is illustrated in plate 1, is well suited for this purpose. Values for the cleavage spacing of the three types of clay minerals common in soil colloids are listed in table 1 together with intensities of the various orders of reflection.

The (001) spacing of montmorillonite varies with water content (17, 23), and this variation can be used as an aid in identification. Irrespective of water content, however, the second most intense reflection has a spacing near

3.0 Å., which is always less than the spacing of the second observed order from kaolinite. This reflection can be confused with the intense third observed order from hydrous mica.

Hydrous mica and kaolinite can be identified with certainty by use of the oriented samples. The mixed layer minerals, however, have a strong reflection with a spacing of about 3.0 Å., and this is confused with that of montmorillonite. As a practical matter, the identification of montmorillonite is difficult because of these confusing factors.

The crystal lattices of kaolinite and halloysite are destroyed by heating, with accompanying loss of water, at lower temperature than are those of montmorillonite and hydrous mica. Resultant changes in diffraction patterns after heating to 500° have been utilized by Kelley and Dore (20) for identifying these various minerals. Though their procedure is very useful, it could be improved by removing the decomposition products of kaolinite resulting from the heating before making x-ray diffraction photographs. As has been indicated, these photographs should preferably be made from oriented samples.

X-ray diffraction patterns of kaolinite and halloysite are closely similar, but recognized mineral specimens of the two give perceptibly different results. The pattern of the kaolin mineral common in soils most closely resembles that of kaolinite. The possible presence of halloysite cannot be eliminated, however, and for this reason no distinction is made between the two which are classed together as kaolinite.

It is desirable to remove the free oxides and hydrous oxides of iron as well as the organic matter before preparing the oriented samples, since these materials both obscure the pattern and interfere with the orientation. Their removal also permits use of Cu K α radiation, in making the diffraction photographs, which is more normally available in x-ray laboratories. Relative amounts of each of the clay minerals present in soil colloids can be estimated from the intensities of reflections given by the oriented samples. The accuracy obtained, however, is low.

A component present in a mixture of the type of soil colloids may not be detected in amounts less than 2 per cent. Only a few tenths of a gram of material is needed for the x-ray work, and if necessary this work can be done on a few milligrams.

Water content of clays and thermal analysis

Water is an essential constituent of all the clay minerals and plays an important part in their structures and behavior. It enters both as H₂O molecules and as (OH) groups, as is indicated by the ideal formulas which are repeated here for the sake of clarity:

Kaolin	$[\text{Al}_2] [\text{Si}_2] \text{O}_5(\text{OH})_4$
Hydrous micas	$\text{K} [\text{Al}_2] [\text{AlSi}_3] \text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$
Montmorillonite	$[\text{Al}_2] [\text{Si}_4] \text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$

All of these minerals show considerable adsorption of water. The amount of adsorbed water, as well as the water between layers of montmorillonite and possibly of hydrous mica, depends upon the humidity. In fact, change in weight of a soil colloid as a function of humidity (2) will probably be useful in detecting montmorillonite and mixed layer minerals containing montmorillonite layers.

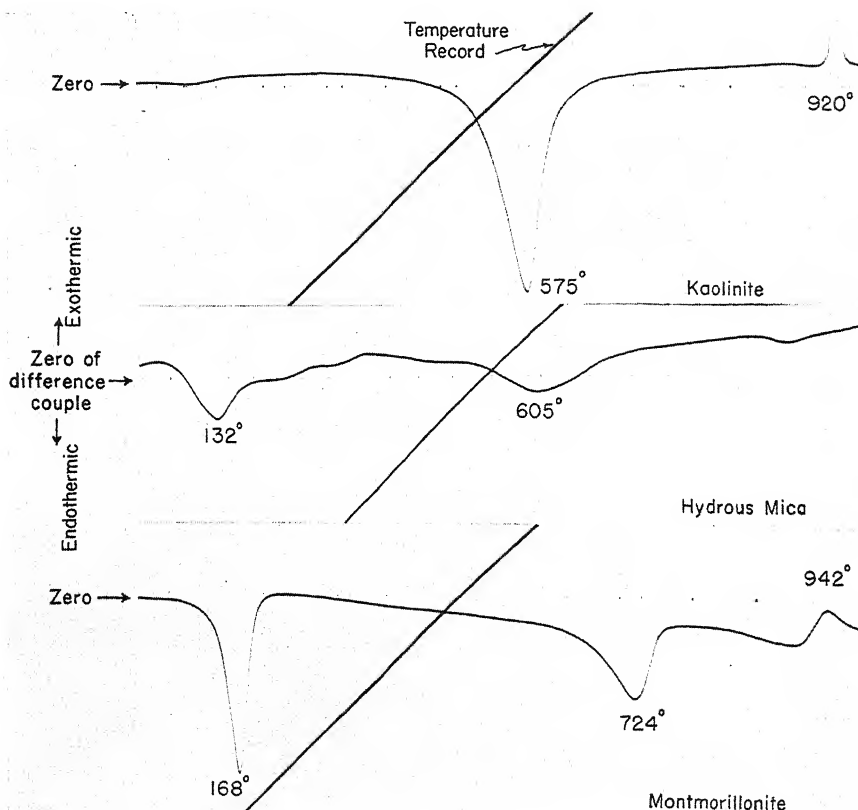


FIG. 1. DIFFERENTIAL THERMAL ANALYSIS CURVES FOR KAOLINITE, HYDROUS MICA, AND MONTMORILLONITE

When clay minerals are heated they lose their water at various temperatures characteristic for each mineral, as shown by Le Chatelier more than fifty years ago (22). Several different methods have been developed for following changes in water content, as a sample is heated. One of these is simply to measure the loss in weight as the sample is heated to constant weight at various temperatures. Another is to follow the change in weight when the specimen is heated at a more or less constant rate (6). Perhaps the simplest is the differential thermal analysis used by Le Chatelier, which is to follow the temperature of a sample relative to that of an inert material as the two are heated at the

same rate. An endothermic change is accompanied by a lag in the temperature of the sample; an exothermic change, by an increase relative to the inert material.

A suitable apparatus for differential thermal analysis patterned after one used by Norton (30), of the ceramics department of the Massachusetts Institute of Technology, is shown in plate 2. The heating rate generally used in this work is from 10–20°C. per minute, and it is necessary to raise the sample to about 1000°C. Both the differential and furnace temperatures are recorded photographically, a suitable type of recording drum being shown in the plate. Small quantities of material are required, less than 0.5 gm. being sufficient.

Differential heating curves for kaolinite, montmorillonite, and hydrous mica, are reproduced in figure 1. The nature of the changes in kaolinite upon heating are discussed as an example. Below 200°C. kaolinite loses adsorbed water endothermically, and there is some incidental change caused by differences in heat capacity, compaction, etc. relative to the inert material. The most characteristic feature is the endothermic loss of water of composition between 550–600°C., and this can safely be used as a criterion for a kaolin material and as a basis for its semiquantitative estimation. After the loss of water the sample is amorphous and the exothermic change between 950–1000°C. accompanies recrystallization of the aluminum oxide as γ Al_2O_3 .

The most characteristic features of the montmorillonites and hydrous micas are their endothermic loss of water below 200°C. and near 700°C. There are considerable variations for different samples at the lower temperature and danger of confusion with adsorbed water. The endothermic reaction of montmorillonite near 700°C. is small compared with that of kaolin near 580°C. and is not sufficiently different from that of hydrous mica to allow an unambiguous distinction between the two.

Although thermal analysis for identification of clay minerals can be applied to the untreated soil, as has been done, for instance, by Agafanov and Jouravsky (1) for a group of soils from Tunis, it is very desirable to remove the organic matter, since this burns exothermically over a wide region, sometimes obscuring kaolinite. It is not absolutely necessary to separate the colloid, especially in heavy soils where it is a considerable fraction of the soil.

SUMMARY

The nature and compositions of minerals present in the colloidal fractions of soils are discussed, and methods are described for identifying these minerals. The most common components of soil colloids are kaolin minerals (kaolinite or halloysite), hydrous micas, montmorillonites, quartz, goethite, and hematite. These can be identified and their amounts estimated by simultaneous use of suitable chemical analyses, x-ray observations, and behavior upon heating. X-ray measurements, though desirable, are not indispensable, and methods,

although somewhat inadequate, for identification of clay minerals can readily be carried out in most soil laboratories.

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PLATE 1

CAMERA FOR MAKING X-RAY DIFFRACTION PHOTOGRAPHS OF ORIENTED SAMPLES

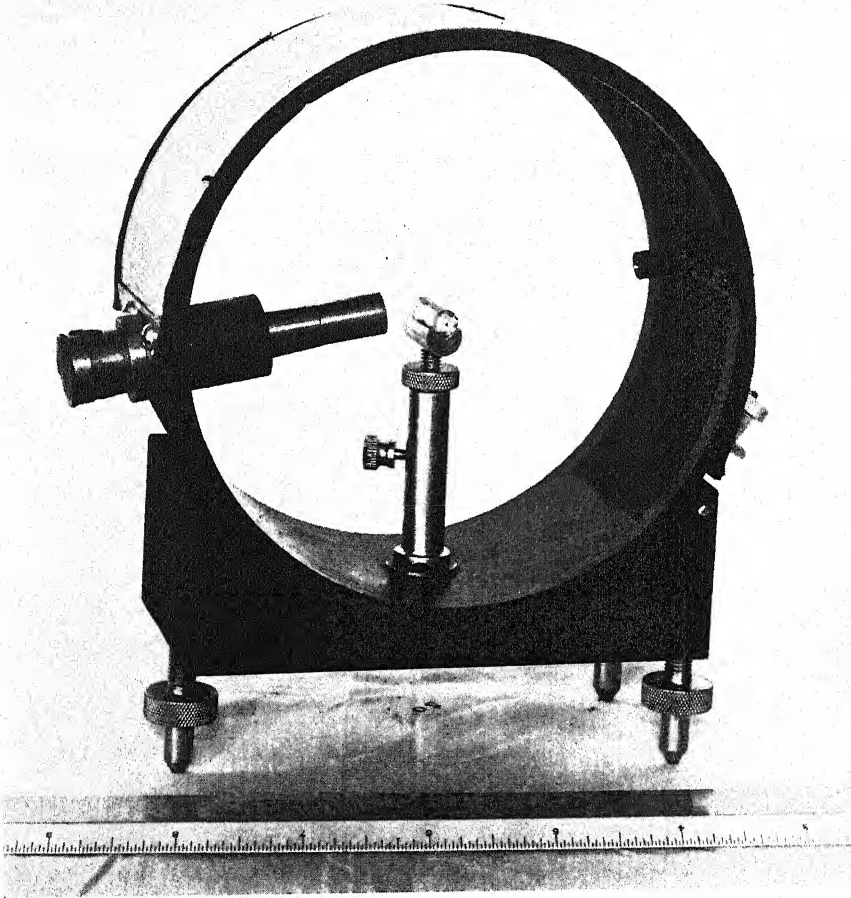
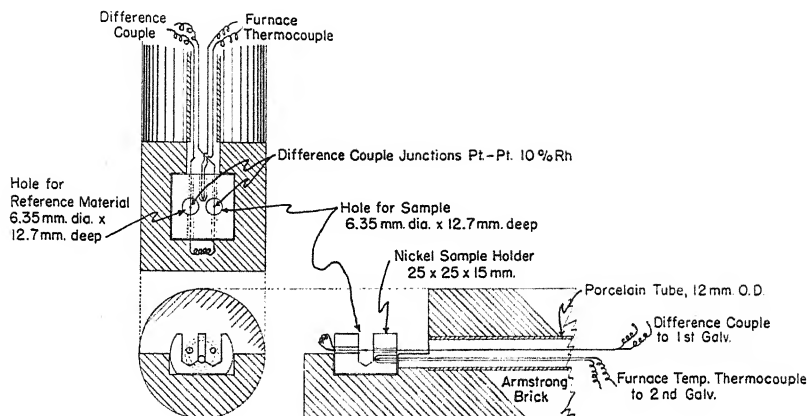
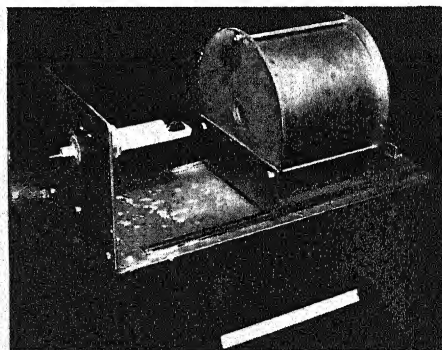
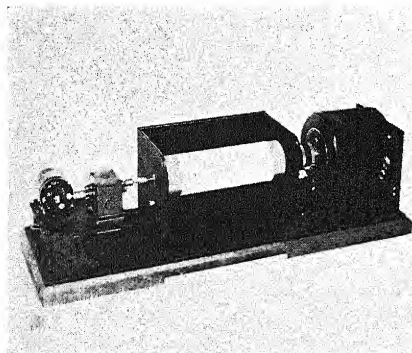
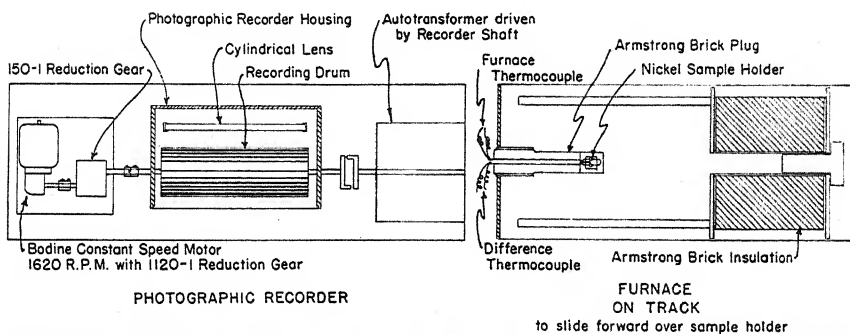


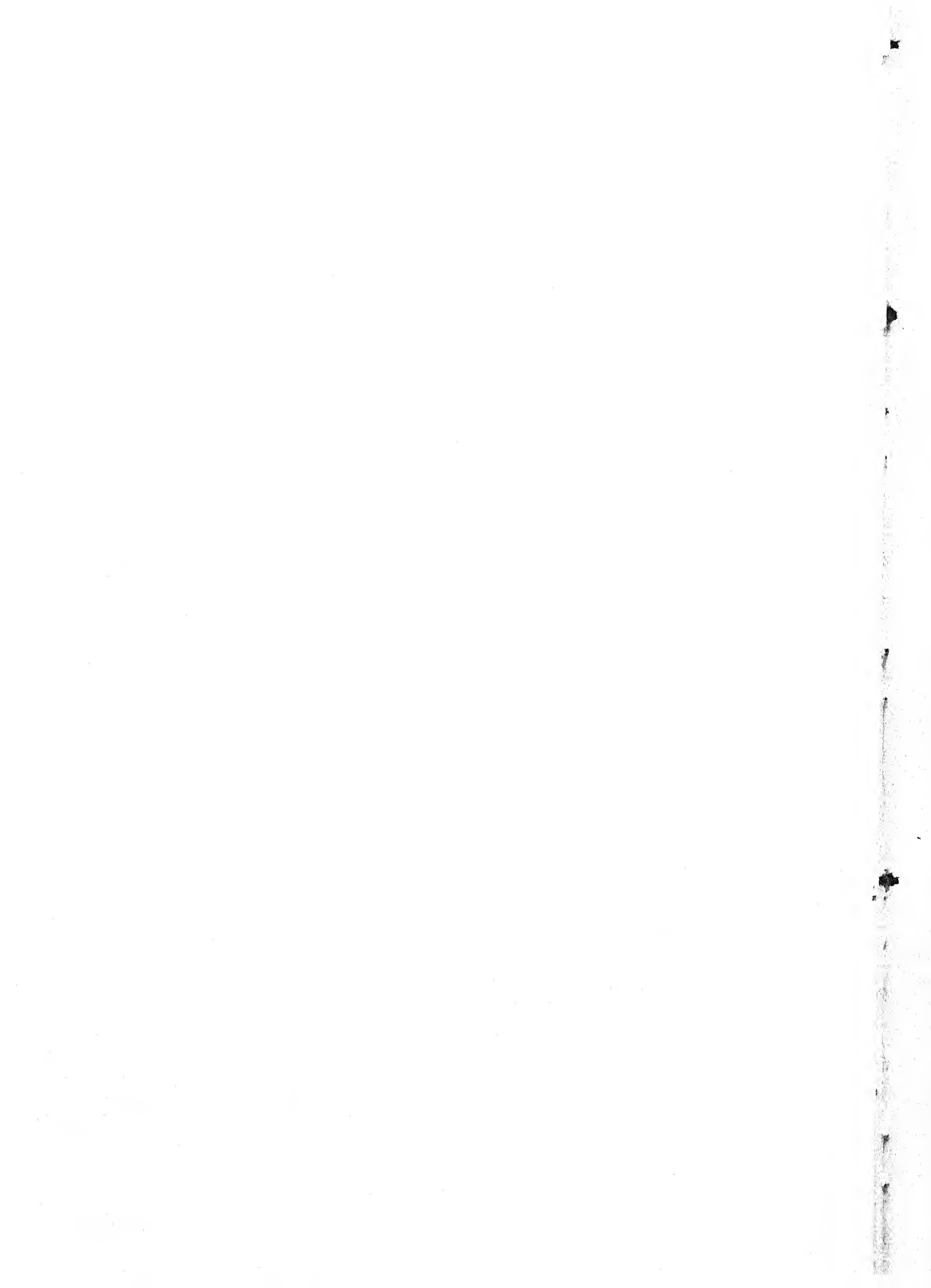
PLATE 2

APPARATUS USED FOR DIFFERENTIAL THERMAL ANALYSIS



DETAIL OF SAMPLE HOLDER





MINERALS PRESENT IN SOIL COLLOIDS: II. ESTIMATION IN SOME REPRESENTATIVE SOILS

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Methods for identifying mineral components of soil colloids described in the previous paper are here applied to a group of colloids separated from some soils of the continental United States. The colloids examined were from soils of five different great groups. These included a number of red podzolic and gray-brown podzolic soils, and a representative of the prairie, chernozem, and desert great groups. In general, the colloid studied was extracted from the B₂ horizon, but several horizons of the Chester and desert soils were examined. Locations, classifications, and natures of parent rocks from which the soils were derived are listed in table 1. References are given in table 1 to sources of fuller descriptions, locations, and analytical data other than those obtained in this work.

Examinations were carried out on material having an effective diameter of less than 0.3 μ , which was separated from aqueous suspensions by a high-speed centrifuge. This fraction usually amounts to about 75 per cent of the material smaller than 2 μ , the quantity of which in the various soils, as determined by mechanical analysis, is listed in table 3.

Chemical analyses useful in identifying minerals of the colloid fraction are given in table 2. Ignition losses at various temperatures and determinations of free and combined Fe₂O₃ were carried out in the course of this work. The remainder of the analyses were taken from the references cited in table 1. Those constituents considered unessential for identifying the principal components of the colloidal fractions are omitted from the table.

Estimates of amounts of various minerals present, based on analytical, x-ray diffraction, and thermal methods, are listed in table 3, together with a composite estimate based on all three methods. The principal components found are some of those described in the preceding paper, specifically, kaolinite, hydrous mica, and free oxides and hydrous oxides of iron.

The best estimate of the amount of iron present as oxides and hydrous oxides is obtained from the chemical analyses. It must be borne in mind, however, that the chemical method for determination of free oxides and hydrous oxides does not differentiate between amorphous and crystalline material. Though

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TABLE 1
Sources of soil colloids used

SOIL SERIES AND LOCATION	GREAT GROUP	PARENT ROCK	REFERENCE DESCRIBING SOURCE*
Cecil, Iredell Co., N. C.	Red podzolic	Granitic	1
Greenville, Dougherty Co., Ga.	Red podzolic	Coastal plain, interbedded with limestone	2
Decatur, Franklin Co., Ala.	Red podzolic	Limestone	2
Dewey, Franklin Co., Ala.	Red podzolic	Limestone	2
Fullerton, Cherokee Co., Ala.	Yellow podzolic	Cherty limestone	2
Frederick, Rockbridge Co., Va.	Gray-brown podzolic	Limestone	2
Hagerstown, Center Co., Pa.	Gray-brown podzolic	Limestone	2
Hagerstown, Washington Co., Md.	Gray-brown podzolic	Dolomitic limestone	2
Hagerstown, St. Francis Co., Mo.	Gray-brown podzolic	Limestone	2
Chester, Montgomery Co., Md.	Gray-brown podzolic	Granitic	3
Manor, Fairfax Co., Va.	Gray-brown podzolic	Granitic	3
Miami, Grant Co., Ind.	Gray-brown podzolic	Glacial till	1
Carrington, Buchanan Co., Ia.	Prairie	Glacial till	1
Barnes, Grant Co., S. D.	Chernozem	Glacial till	1
Desert soil, Kern Co., Cal.	Desert	Granitic	4

* 1, U. S. Dept. Agr. Tech. Bul. 484; 2, *Ibid* 678; 3, *Ibid* 609; 4, Soil Sci. Soc. Amer. Proc. 3 (1938).

TABLE 2
Chemical analyses of soil colloids

SAMPLE NUMBER	SOIL SERIES	HORIZON	K ₂ O	MgO	Al ₂ O ₃	Fe ₂ O ₃		SiO ₂	H ₂ O HELD AT	
						Combined	Free		100°C.	300°C.
			per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
C9418	Cecil	C	0.04	0.22	30.5	2.1	15.4	35.1	12.4	9.4
C1067	Greenville	B ₂	0.07	0.35	34.6	1.6	10.4	38.8	12.1	10.4
C125	Decatur	B ₂	0.88	1.03	31.3	1.5	13.3	39.1	10.9	8.8
C120	Dewey	B ₂	0.84	1.00	31.3	1.1	12.7	40.4	10.4	8.6
C109	Fullerton	B ₂	1.28	1.07	27.2	1.6	7.7	49.8	9.4	7.4
C810	Frederick	B ₂	1.22	1.23	32.6	1.0	10.5	40.3	11.3	9.3
C801	Hagerstown (Pennsylvania)	B ₂	1.45	1.34	32.5	1.5	8.9	41.4	11.1	9.2
C805	Hagerstown (Maryland)	B ₂	2.30	2.18	30.0	2.0	7.6	43.2	10.4	7.8
C1486	Hagerstown (Missouri)	B ₂	1.61	1.62	27.1	3.5	7.0	46.7	9.4	6.7
C1671	Chester	A ₂	1.71	1.08	29.5	2.5	10.8	38.6	10.0	7.5
C1672	Chester	B ₂	1.58	1.11	27.4	2.6	15.0	39.0	10.9	7.4
C1673	Chester	C	1.44	0.97	27.6	2.5	17.7	36.5	11.1	7.3
C814	Manor	B ₂	1.53	0.92	30.3	2.6	10.1	40.3	10.6	7.8
C10343	Miami	B ₂	4.37	2.09	23.4	4.4	7.1	47.1	7.8	4.7
C10086	Carrington	B ₃	1.85	1.81	24.3	4.0	9.7	45.4	9.6	6.4
C10307	Barnes	B ₂	1.44	2.68	19.4	9.8	0.0	49.2	7.2	5.6
C3420	Desert soil*	B ₁	1.99	2.91	25.4	7.6	2.8	47.5	8.9	7.0
C3421	Desert soil*	B ₂	1.67	2.97	24.2	8.9	2.2	48.0	8.9	6.7
C3422	Desert soil*	B ₃	0.87	3.30	22.5	8.4	2.4	49.5	8.9	6.4
C3423	Desert soil*	C	0.70	3.41	22.0	7.7	2.0	50.1	8.8	6.4

* This soil has not yet been correlated but is very similar to soils of the desert group

the x-ray method gives some evidence of the nature of the iron oxide, it cannot be used as the basis for an estimate, and thus does not eliminate the possible

TABLE 3
Estimates of mineral components of soil colloids

SAMPLE NUMBER	SOIL SERIES	ANALYTICAL		X-RAY				THERMAL ANALYSIS, KAOLIN	COMPOSITE ESTIMATES*						CLAY (2 μ) BY MECHANICAL ANALYSIS
		Hydrous mica	Free iron oxides	Kaolin	Hydrous mica	Montmorillonite	Cryst. iron oxides		Kaolin	Hydrous mica	Montmorillonite	Free iron oxides	Quartz and calcite†		
C9418	Cecil	Abs.	15	80	Abs.	Abs.	G.H.†	80	80	0	0	15	10 quartz	44	
C1067	Greenville	Abs.	10	80	Abs.	Abs.	G.H.	90	90	0	0	10		42	
C125	Decatur	>10	13	80	10	Abs.	G.H.	50	70	10	0	13		49	
C120	Dewey	>10	13	80	10	Abs.	G.H.	60	70	10	0	13		36	
C109	Fullerton	>25	8	70	30	Abs.	G.	70	60	20	0	8		49	
C810	Frederick	>25	10	70	20	Abs.	G.	70	70	20	0	10	5 quartz	70	
C801	Hagerstown (Pennsyl- vania)	>25	9	70	20	Abs.	G.H.	70	70	20	0	9		53	
C805	Hagerstown (Maryland)	>50	8	50	50	Abs.	G.H.	50	50	40	0	8		70	
C1486	Hagerstown (Missouri)	>25	7	50	50	Abs.	G.	40	40	40	0	7		39	
C1671	Chester	>25	11	60	30	Abs.	G.H.	40	50	30	0	11		20	
C1672	Chester	>25	15	60	30	Abs.	G.H.	40	50	30	0	15	23		
C1673	Chester	>25	18	60	30	Abs.	G.H.	40	50	30	0	18	17		
C814	Manor	>25	10	60	30	Abs.	G.H.	50	50	40	0	10	24		
C10343	Miami	>75	7	10	80	10	10	80	0	7	51		
C10086	Carrington	>25	10	50	30	10		30	40	40	10	10	24		
C10307	Barnes	>25	0	30	40	20	20	30	40	20	0	6 calcite	36	
C3420	Desert soil	>50	3	20	80§	20	20	70§	3		36		
C3421	Desert soil	>25	2	20	80§	20	20	70§	2		33		
C3422	Desert soil	>10	2	20	80§	20	20	70§	2		30		
C3423	Desert soil	>10	2	20	80§	20	20	70§	2		14		

* The authors have made no attempt to make these add to exactly 100, since the values are inexact.

† Amounts of quartz were estimated from the x-ray diffraction patterns; and calcite, from chemical analyses. Quartz present in amounts less than 5 per cent is not indicated because of uncertainty of identification.

‡ G. and H. indicate the presence but not the amounts of goethite and hematite respectively.

|| Some unknown iron-bearing component, about 10 per cent.

§ The principal mineral present in these soil colloids is of the mixed layer type.

presence of amorphous material. Actually, both goethite and hematite were identified from the x-ray diffraction patterns, as indicated in table 3.

In some colloids free hydrous oxides of iron are indicated by thermal analysis, as illustrated in figure 1, but the method does not appear trustworthy for estimating their amounts. In fact, the temperatures at which such hydrous materials in the colloids lose their water of composition seem to be very variable over the region 275–375°C. Moreover, the endothermic effect is not so great as would be expected from the probable amounts of goethite present. Thermal analysis of the colloid from the Cecil soil indicated the presence of a small amount of goethite even after the usual treatment for removing free oxides and

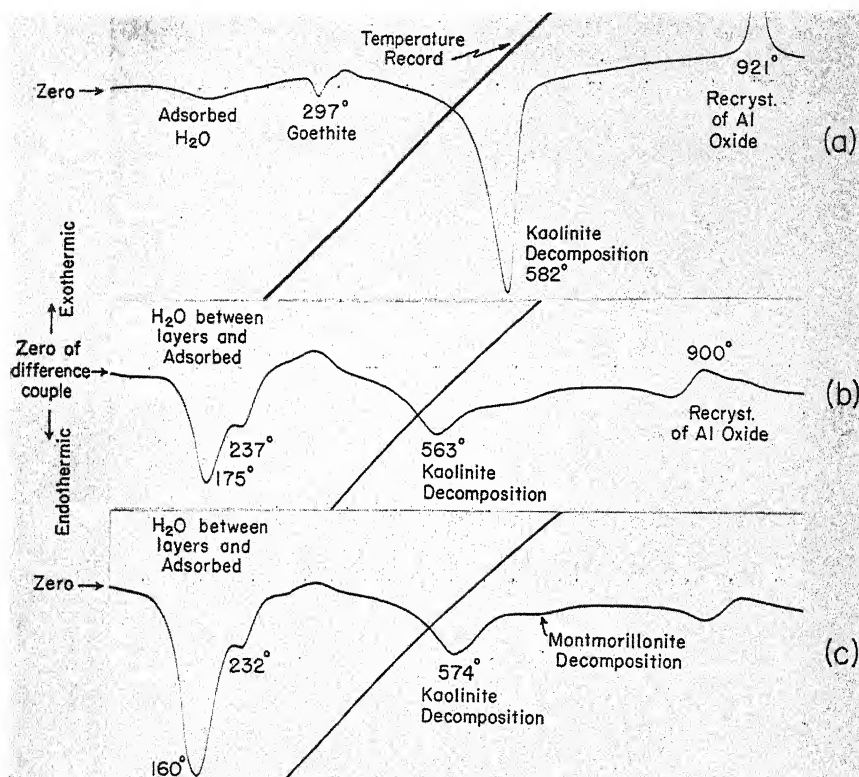


FIG. 1. DIFFERENTIAL THERMAL ANALYSIS CURVES FOR (a) CECIL, (b) DESERT, AND (c) BARNES SOIL COLLOIDS

hydrous oxides of iron. For this reason the amounts of combined iron indicated in table 2 include any small amounts of undissolved oxides.

The amount of K₂O obtained by chemical analysis is a good criterion for estimating the minimum quantity of hydrous mica, as this is the only mineral present that contains potassium. In making the estimate in the third column of table 3, it was assumed that hydrous mica contains 5 per cent K₂O. This estimate is considered to be a minimum one because hydrous mica present in the various colloids might contain less than 5 per cent K₂O but probably

not more than that amount. It was pointed out in the preceding paper that the amounts of magnesium, combined iron, and water loss at various temperatures give a method for rough qualitative identification of hydrous mica and montmorillonite, and this can be seen by inspection of tables 2 and 3.

Estimates of kaolinite, hydrous mica, and montmorillonite, determined by x-ray diffraction from oriented samples, are listed in table 3. Such estimates are quite approximate, as they are based upon visual comparison of intensities. They depend, moreover, upon the various minerals orienting without preference, which seems to be the case in samples free of organic matter and of free oxides and hydrous oxides of iron. The x-ray method gives a more absolute value for estimating the amounts of hydrous mica present than does the chemical analysis. In general, however, the minimum amount of hydrous mica indicated by the chemical analyses is in agreement with the amount as estimated from x-ray diffraction patterns.

Montmorillonite was identified only in the colloids from the Barnes soil and possibly the Carrington soil. The predominant constituent of the colloids separated from the desert soil can best be described as a mixed layer mineral of the type discussed in the preceding paper. In these colloids the mixed layer mineral is probably composed of montmorillonite and hydrous mica layers. The coarser fractions of the soil contain a mineral that is essentially identical, except for particle size, with that of the colloid.³

The amount of kaolinite present in a sample can best be determined by thermal analysis. Agreement with estimates based on x-ray diffraction are not so close as might be desired, but both methods are subject to considerable refinement if necessary. As different samples varied greatly in apparent densities, it was necessary to vary the weight used for thermal analysis, since the volume was maintained constant. The method was standardized against pure kaolinite.

Differential heating curves obtained from the Cecil, desert, and Barnes soil colloids are shown in figure 1, and some features of interest are indicated. These curves can be compared with those of clay minerals by referring to the preceding paper. The endothermic change accompanying decomposition of kaolinite near 580°C. is apparent for each soil colloid. The area of this endothermic region was used in estimating the amount of kaolinite, and it perhaps is evident that measurement of the area could not be very accurate, particularly where the amount of kaolinite is small.

X-ray diffraction patterns indicate the presence of quartz in a number of the samples, the greatest amount being in the colloid separated from the Fullerton soil, which contained about 10 per cent. The Hagerstown (Missouri) soil colloid contained about 5 per cent quartz, and the remainder of the samples less than this amount. Small quantities of quartz cannot be identified with

³ Drosdoff, M., and Miles, E. F. 1938 Action of hydrogen peroxide on weathered mica. *Soil Sci.* 46: 391-396.

certainly in the presence of considerable hydrous mica, because the strongest diffraction line of the former is very close to a moderately intense line of the latter. As mentioned in the preceding work, the amount of quartz present in some samples depends, in a large measure, on the upper size limit chosen in separating the colloid. Its presence in considerable quantities vitiates any use of $\text{SiO}_2:(\text{R}_2\text{O}_3 + \text{RO})$ ratios in drawing conclusions about the nature of clay minerals present.

X-ray diffraction patterns of the colloid separated from the Carrington soil showed a minor component that could not be identified with certainty. It was removed by the treatment given in the determination of the free iron oxides and thus supposedly is a compound rich in iron. The possibility of this unknown component's being goethite could not be eliminated with certainty. As a matter of fact, the diffraction pattern of goethite does not contain lines of sufficient intensities to permit the ready identification of this mineral in mixtures in which it is a minor component.

Chemical analyses of the colloid separated from the Barnes soil showed that it contained about 6 per cent calcium carbonate. X-ray diffraction patterns of this untreated soil colloid, which contained about 2 per cent organic matter, were poor, and gave a meager, but positive, evidence for the presence of calcite. The chemical method, of course, is the best one for estimating calcium carbonate.

DISCUSSION

The properties of the inorganic colloidal fraction of soils are necessarily determined by the characteristics and amounts of the component minerals. Attempts to identify and to estimate these minerals have been based chiefly upon chemical analysis. With the background of mineralogical information now available, which was briefly outlined in the preceding paper, the significant analyses for mineral identification are evident.

Tables 2 and 3 show that potassium is present in considerable amounts only when hydrous mica is one of the components. The Cecil and Greenville colloids, both of which contain less than 0.1 per cent K_2O , contain no detectable amounts of hydrous mica. On the other hand, the Miami colloid, which is largely hydrous mica, contains the greatest amount of potassium, 4.4 per cent K_2O . A similar but less striking relationship is indicated by the amount of combined Fe_2O_3 and MgO , as well as by the H_2O held at 300°C . This temperature was selected as being sufficiently high to drive off adsorbed water and the swelling water of montmorillonite, but not so high as to cause much decomposition of the kaolinite.

Attention has been directed to the caution that must be exercised in the use of $\text{SiO}_2:(\text{R}_2\text{O}_3 + \text{RO})$ ratios for identifying clay minerals. An excellent illustration is afforded by the data given in table 2 for the Carrington and Miami colloids. The $\text{SiO}_2:(\text{Al}_2\text{O}_3 + \text{combined Fe}_2\text{O}_3 + \frac{2}{3} \text{MgO})$ ratios of these colloids are 2.6 and 2.7, respectively, though their mineralogical com-

positions are very different, the former containing about 40 per cent kaolinite and 40 per cent hydrous mica, the latter about 10 per cent kaolinite and 80 per cent hydrous mica. These differences are correctly indicated by the potassium content and the amount of water held at 300°.

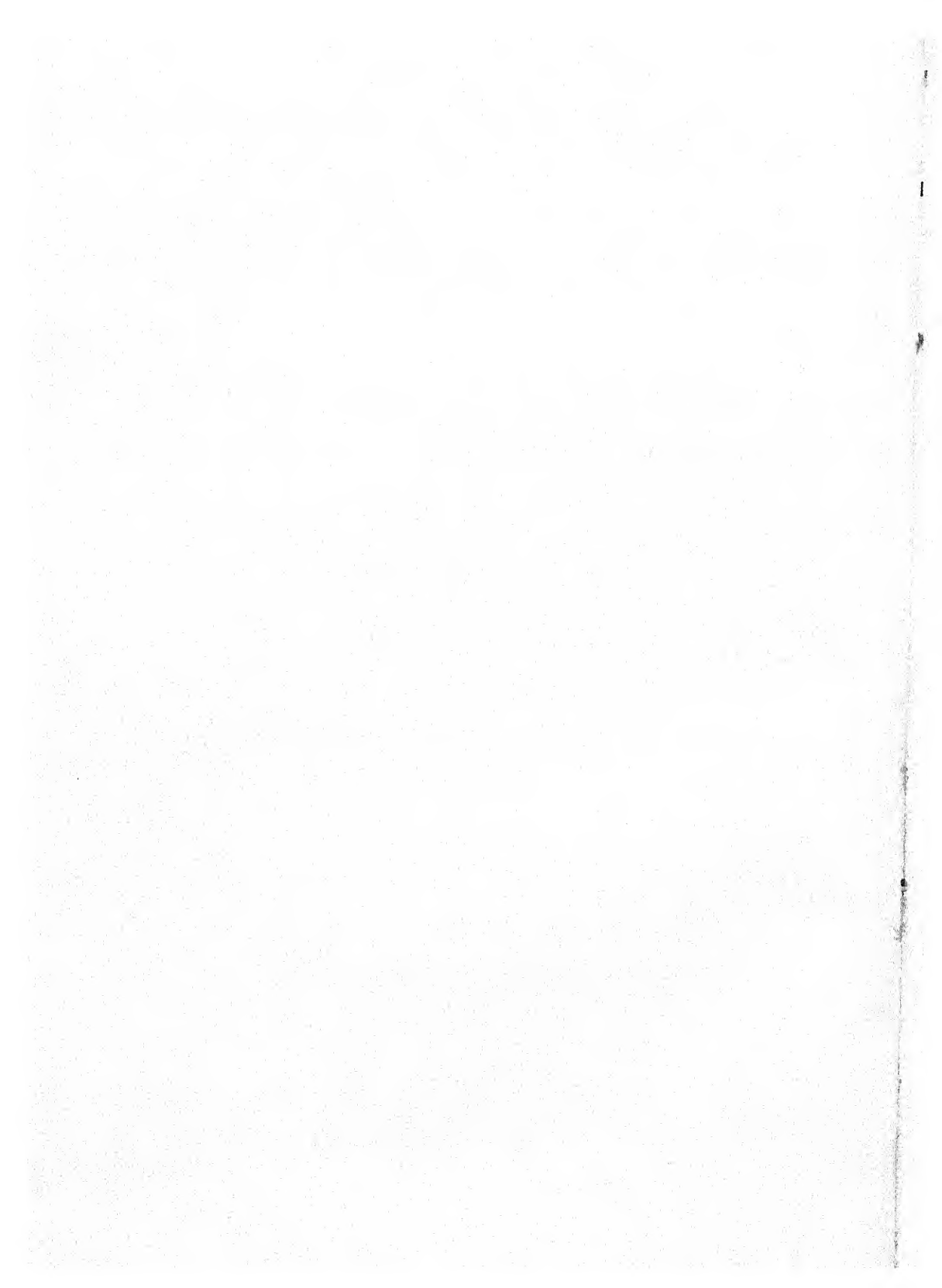
The most serious limitation of chemical data is that they do not permit quantitative estimations and will not detect the presence of minor amounts of kaolinite. Thermal analysis supplements the chemical information, in that it gives the best basis for determining the amount of kaolinite. Use of these two methods gives a fairly satisfactory basis for estimating the component minerals of a soil colloid.

X-ray diffraction data, of course, have served as the basis for the entire development and give a method for estimating all of the components save the free oxides and hydrous oxides of iron. Estimates by the various methods are in essential agreement. The values listed in table 3 have been rounded off so as to indicate their probable accuracies.

The number of samples examined in this work is not sufficiently extensive to warrant general discussion of the relationships between mineral composition of a colloidal fraction and classification of a soil. Results obtained, however, indicate prominent differences between colloids from the B horizons of some different soil groups. Data presented in table 3 suggest that red podzolic soil colloids contain kaolinite as the predominant components, accompanied by large amounts of hydrous oxides and free oxides of iron. Very red soils owe their color to the presence of hematite, as is well illustrated by the Decatur. Gray-brown podzolic soil colloids contain both kaolinite and hydrous mica as prominent components, accompanied by appreciable amounts of free oxides and hydrous oxides of iron.

SUMMARY

Minerals present in the colloidal fraction of 15 soils from continental United States have been identified and their amounts estimated by use of the chemical, thermal, and x-ray diffraction methods discussed in the preceding paper. Kaolinite and free oxides and hydrous oxides of iron were the predominant components of the red podzolic soils examined. Gray-brown podzolic soil colloids contained these minerals associated with appreciable amounts of hydrous mica. Single examples of colloids separated from soils of the chernozem, prairie, and desert group groups were studied.



THE ADSORBED IONS OF COLLOIDAL CLAY AS A FACTOR IN NITROGEN FIXATION BY AZOTOBACTER¹

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Soil microorganisms obtain their mineral nutrients from the colloidal clay fraction, which also is active in controlling and maintaining the supply of ions. Soil microorganisms may also derive mineral nutrients by the breakdown of or exchange from the organic colloid.

Previous studies have shown that colloidal clay will serve to supply adsorbed ions to plants (1, 3) to nitrifying bacteria (2) and to legume bacteria (7, 8). The extent, however, to which the colloidal clay will nurture various microbial populations in the soil is not yet known.

The purpose of this study is to show, first, that colloidal clay will supply *Azotobacter* with adsorbed ions, the nature of which influences nitrogen fixation directly; second, that adsorbed ions in a medium exert an influence differing from the influence of ions in solution; and third, that the nature of the colloidal material alone influences nitrogen fixation.

EXPERIMENTAL

The influence of nutrients in solution and of adsorbed nutrients on colloidal clay was studied first. Electrodialyzed hydrogen clay in aqueous suspensions of 2.5 per cent served as a base to which were added different ions. All nutrients were added in the order given in table 1, and sufficient time was allowed between additions of nutrients and use to permit the reaction to reach completion.

The calcium medium, as outlined in table 1, simulated a good soil. Other variable conditions were represented in the remaining media. The magnesium media had varying amounts of magnesium with constant amounts of calcium, potassium, and phosphorus, the variation in magnesium being balanced with reciprocal variations in barium additions. The media to which the strontium had been added, as outlined, had a constant amount of calcium, potassium,

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and phosphorus, but had varying amounts of strontium and reciprocal amounts of magnesium. To 100-ml. portions of each of the media was added 2 gm. of mannitol. The media were then sterilized, inoculated with *Azotobacter*, and aerated for 3 days by forcing sterile air through the suspension.

TABLE 1
Colloidal-clay media of different mineral levels

COMPONENTS OF MEDIA	DIFFERENT MEDIA AND DESIGNATING SYMBOLS								
	Ca	Mg I	Mg II	Mg III	Mg IV	Sr I	Sr II	Sr III	Sr IV
Magnesium	2.00								
Calcium		2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Phosphorus	4.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Potassium	3.33	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Calcium	11.93								
Barium			4.05	6.25	9.38				
Magnesium		12.50	8.45	6.25	3.12	8.45	6.25	4.05	
Strontium						4.05	6.25	8.45	12.50
Mannitol		20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
H-clay		25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Water to make 1000 ml.									

TABLE 2
Nitrogen fixed by Azotobacter in colloidal clay with different adsorbed ions

MEDIA	NITROGEN FIXED PER 100 ML. CLAY			pH OF MEDIUM		
	First trial	Second trial	Mean	Autoclaving		After growth
				Before	After	
	mgm.	mgm.	mgm.			
Ca.....	12.73	14.36	13.54	6.44	6.44	6.63
Mg I.....	8.68	8.73	8.70	7.15	7.15	6.60
Mg II.....	3.59	4.18	3.88	7.00	7.16	6.70
Mg III.....	2.93	2.54	2.73	7.27	7.36	6.90
Mg IV.....	0.37	2.05	1.21	7.44	7.49	7.24
Sr I.....	12.50	13.20	12.85	6.60	6.60	6.40
Sr II.....	14.10	14.10	6.62	6.50	6.60
Sr III.....	13.20	13.90	13.55	6.84	6.90	6.91
Sr IV.....	12.50	10.60	11.55	7.05	7.10	7.05

In order to observe the influences of ions adsorbed on colloids and of ions in solution upon the fixation of atmospheric nitrogen by *Azotobacter*, Ashby's medium (4) was prepared with the following concentrations of various substances and served as a control medium throughout the experiment: mannitol, 15 gm.; MgSO_4 , 0.2 gm.; KH_2PO_4 , 0.2 gm.; NaCl , 0.2 gm.; CaSO_4 , 0.1 gm.; CaCO_3 , 5.0 gm.; water to make 1000 ml.

To portions of the control medium were added concentrations of from 1 to 2.5 per cent of the following colloids: H-clay, bentonite, zeolite, permutite, and norite. The H-clay colloid was usually centrifuged out of suspension and added to the Ashby's medium in concentration of 2.5 per cent. In one instance the Ashby's medium was filtered to remove all sediment, and the H-clay was added to the filtrate. Although the Ashby's filtrate originally was neutral, it became distinctly acid upon the addition of the H-clay. The medium was then brought to neutrality by the addition of NaOH.

The bentonite, permutite, norite, and zeolite colloidal systems were prepared by adding the finely divided material to Ashby's medium. The total nitrogen was determined by the Kjeldahl method. The results given in table 2 represent the mean of duplicate or quadruplicate determinations of 3 days' growth. All figures were corrected against checks.

RESULTS

The best fixation of atmospheric nitrogen by *Azotobacter* in this first experiment occurred with a high level of magnesium, in the case of the barium and magnesium series, prepared by adding only sufficient ions to replace the exchangeable hydrogen. A 25 per cent decrease of exchangeable magnesium with a similar increase of exchangeable barium decreased nitrogen fixation by 50 per cent. When the magnesium was further decreased 25 per cent, nitrogen fixation dropped an additional 25 per cent. A further decrease of magnesium resulted in some additional decrease of nitrogen fixation (table 2).

In the series of media in which there were constant amounts of calcium, potassium, and phosphorus, but variable amounts of magnesium and strontium, fixation of atmospheric nitrogen by the *Azotobacter* was approximately constant. There was a slight increase in fixation when both strontium and magnesium were present. The calcium medium also gave good nitrogen fixation.

When *Azotobacter* was grown for 3 days in Ashby's medium it was capable of fixing an average of 4.6 mgm. of nitrogen per 100 ml. of medium. The mean figure obtained here is slightly below the figures obtained by Gainey (6). Although there was considerable variation in the amount of nitrogen fixed in duplicate samples of Ashby's medium, more consistent values were obtained with the colloidal systems. The wide differences occurring in Ashby's medium alone were perhaps due to a gradual loss in the ability of the organism to fix nitrogen. When 2.5 gm. of H-clay was added to the same medium, the organism fixed 14.38 mgm. per 100 ml.—an increase of 3.1 fold.

Since Ashby's medium contained a large amount of precipitate, it was suspected that the presence of solid material might influence nitrogen fixation. In order to test this hypothesis, *Azotobacter* was grown in flasks of filtered Ashby's medium and in the same medium plus 2.5 gm. of H-clay. The amount of nitrogen fixed was 0.79 gm. per 100 ml. filtered medium, and 6.70 mgm. per 100 ml. when H-clay was added. The clay addition gave an increase of 8.5 fold. It is apparent from these results that the presence of finely divided

material has some physico chemical influence on the fixation of atmospheric nitrogen by *Azotobacter*. These data are shown in table 3.

The addition of 2 gm. of bentonite to 100 ml. of Ashby's medium resulted in a fixation of 11.24 mgm. of nitrogen as compared with only 0.83 mgm. of nitrogen in the Ashby's medium without the colloidal material. The addition of the colloidal material therefore increased nitrogen fixation 13 fold. When

TABLE 3

Nitrogen fixation in Ashby's medium in the presence and absence of colloidal H-clay

TRIALS	NITROGEN FIXED PER 100 ML. MEDIUM			
	Ashby's medium	Ashby's medium + 2.5 gm. H-clay	Filtered Ashby's medium	Filtered Ashby's medium + 2.5 gm. H-clay
	mgm.	mgm.	mgm.	mgm.
First.....	9.00	14.86	0.60	
	8.26	14.86	0.60	
Second.....	4.28	12.52	1.00	6.80
	2.26	12.89	0.67	6.60
Third.....	1.74	16.10	1.04	
	2.06	16.00		
Mean.....	4.60	14.38	0.79	6.70

TABLE 4

*Nitrogen fixation in Ashby's medium supplemented by various colloidal materials**

TRIALS	NITROGEN FIXED PER 100 ML. MEDIUM				
	Ashby's medium	Bentonite	Zeolite	Permutite	Norite
First.....	0.54	9.55	7.20	0	0
	0.40	10.40	7.45	.53	0
Second.....	0.66	12.32	10.10	.23	0
	1.74	12.72	9.80		0
Mean.....	0.83	11.24	8.64	.25	0

* Each supplement added at the rate of 2 gm. per 100 ml. Ashby's medium.

zeolite was added there was a fixation of 8.64 mgm. of nitrogen, a decrease from that in the bentonite medium, yet still more than that in Ashby's medium alone. When permutite or norite was added no significant nitrogen fixation took place, as is indicated in table 4.

DISCUSSION

The natural habitat of *Azotobacter* is the soil, where it obtains its mineral nutrients from the colloidal fraction. Thus it is reasonable to assume that

the energy necessary for the utilization of these nutrients is determined by their concentration at the surface of the colloid. It would seem probable that the mineral nutrients adsorbed at the surface of the colloid, particularly when the colloid is highly saturated, would be much more readily assimilated than those in solution and distributed at random throughout the medium. It is also possible that the colloid may in some way make a favorable physical state for the organism.

From the data, it is apparent that colloidal material influences nitrogen fixation and that the nature of the ions in the adsorption sphere of the colloid play a significant role, as is indicated below.

In Ashby's medium there are considerable insoluble calcium carbonate and some insoluble calcium phosphate. These materials, although finely divided, do not long remain suspended except when air is forced through the solution. As the results indicate, the presence of suspended material in Ashby's medium aids in the fixation of nitrogen, either through some physical factor or by replenishing ions to the solution as they are removed by the growing organisms. In the filtered Ashby's medium, where there is no insoluble precipitate to replenish ions taken by the organisms in their metabolism, the nutrients become less concentrated as the mineral needs of the organism are met. If, however, a colloidal material such as hydrogen clay or bentonite is added, the nutrients are concentrated in an available form, and nitrogen fixation is increased significantly. In the unfiltered Ashby's medium the exchange capacity of added colloid is saturated from the ions already in solution. This causes more ions to go into solution from the insoluble portion of the medium. The organism can then satisfy its mineral needs from the easily available exchangeable ions of the colloid. In the filtered Ashby's medium, apparently, insufficient ions remain to satisfy the base exchange capacity of the colloid, and for this reason the filtered medium does not function so well as does the unfiltered medium. It seems probable that the superiority of the colloidal medium over Ashby's medium may be due to the fact that the ions adsorbed at the surface of the colloid are concentrated in a limited area. The removal of a few of the adsorbed ions does not greatly influence the growth of the organism because there is still a large reserve of available ions in the adsorption sphere of the colloid.

Each gram of colloidal clay had a water of hydration content of 5.2 gm. (5). Since each 100 ml. of medium contained 2.5 gm. of clay, that means that 13 ml. of each 100 ml. was water of hydration. In other words, the entire mineral content of the 100 ml. of medium was concentrated in 13 ml. or less. It is entirely possible that the organism can obtain its mineral needs from 13 ml. more easily than it can get the same needs from 100 ml. As the data indicate, the addition of clay to Ashby's medium increased nitrogen fixation by 3.1 fold. Thus by concentrating the nutrients of the medium 7 fold on colloidal clay, the nitrogen fixation was increased 3.1 fold.

CONCLUSIONS

Colloidal clay served successfully as a basic medium for the fixation of atmospheric nitrogen by *Azotobacter*.

The amount of nitrogen fixed was influenced by the kind and quantity of ions adsorbed by the clay.

The addition of colloidal material such as colloidal clay to an aqueous medium with minerals enhanced the ability of the *Azotobacter* to fix atmospheric nitrogen.

Certain colloids when added to the Ashby's medium appeared to be more effective than others in encouraging fixation of atmospheric nitrogen by the *Azotobacter*. The order of effectiveness of those tested was as follows: clay colloid, bentonite, zeolite, permutite, norite.

Suspended solid material did not serve as effectively as colloidal material with a base exchange capacity.

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THE NITRIFICATION OF AMMONIUM THIOCYANATE (A WEED ERADICANT) AND THE EFFECT OF THIS COMPOUND UPON THE SOIL POPULATION¹

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In recent years interest in the use of chemical weed eradicates has increased. Sodium chlorate alone or in mixtures with other substances has been widely used and has been found effective in killing the most persistent weeds. The use of chlorate, however, requires extreme care in application because of the very decided danger of explosion and fire. Harvey (6) has suggested the use of ammonium thiocyanate, which he has found to be a useful eradicator. This compound can be made cheaply as a by-product of gas manufacture, is non-explosive, and creates no fire hazard; in addition, 18 per cent by weight of the substance is ammoniacal nitrogen, and an equal amount is cyanate nitrogen. Though there is no doubt that ammoniacal nitrogen as such, or after nitrification, is an excellent nitrogenous fertilizer, there is little information as to the availability of the nitrogen in the thiocyanate radical.

Not only should the availability of the thiocyanate nitrogen be investigated, but before ammonium thiocyanate can be recommended as a weed eradicator, later to yield nitrogenous fertilizer, studies on its toxicity to plants and also the "partial sterilization" effects on the soil should be made. Harvey has been carrying on extensive investigations on ammonium thiocyanate as a weed eradicator and on its toxic effect on the soil, together with certain other physiological aspects of the problem.

The experiments reported in this paper were carried out to determine the effect of additions of thiocyanate on the soil microflora and on the important soil biochemical processes, nitrification. It seemed that the course of the transformation of the nitrogen from the thiocyanate radical to ammonia or nitrates, which are directly available to plants as nitrogen sources, should indicate how valuable this compound might be expected to become as a nitrogen fertilizer. Pot and field experiments should follow this work.

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EXPERIMENTAL

Air-dried sieved soil was placed in tumblers in 200-gm. quantities. Water was added to bring the moisture content to about two-thirds saturation, which was maintained throughout the experiment. To some of the tumblers different amounts of c.p. ammonium thiocyanate or sodium thiocyanate were added with the water. As shown in the tables, various types of soil were used. At certain intervals, bacterial counts were made by Waksman's technic (9), using sodium albuminate agar as described by Fred and Waksman (2). Ten replicate plates from each dilution were usually poured, but all the plates could rarely be counted because of the prevalence of molds. No plates with any appreciable mold growth were counted.

These tumblers were incubated at 28°C. for various lengths of time. Tables 1, 2, and 3 show the results.

TABLE 1
Bacterial count ($\times 100,000$) of sandy loam garden soil

INCUBATION TIME	CONTROL	1.25 GM. NH_4CNS PER 100 GM. AIR-DRIED SOIL	1.25 GM. NaCNS PER 100 GM. AIR-DRIED SOIL
<i>weeks</i>			
3	71.6	21.2	36.8
5	57.6	8.4	13.0

TABLE 2
Bacterial count ($\times 100,000$) of clay garden soil

INCUBATION TIME	CONTROL	0.125 GM. NH_4CNS PER 100 GM. AIR-DRIED SOIL	0.125 GM. NaCNS PER 100 GM. AIR-DRIED SOIL
<i>weeks</i>			
7	68.5	50.4	46.0
9	128.8	26.0	45.0

The tables show averages of all the plates counted from the dilution. In order properly to interpret data obtained from poured plates, either all replicate counts or the values of the means and certain statistical findings should be given. Variation in counts of plates was greater than generally should be obtained. This was ascertained by using Fisher's (1) method with small samples for counts of bacterial colonies. Although variation shown by this statistical analysis is admittedly large, very few data on bacterial counts have shown less variation. In testing whether the counts from ammonium thiocyanate and sodium thiocyanate treated soils are sufficiently different from those of the untreated soil, Fisher's method of determining the significance of differences between means of small samples shows that in all cases but one, P is less than 0.01. As the highest value of P usually taken to show significance is 0.05, the results here obtained indicate that the differences for each

week between the numbers of bacteria in the thiocyanate-treated and untreated soils are significant. The only exception where P is less than 0.5 is in the 7-week period of table 2. Here there is no significant difference between thiocyanate-treated and untreated soils. It is worth noting that this one case of no significance is with soils treated with less cyanate than that applied to soils showing a depression of bacterial numbers, and with more cyanate than that applied to soils showing a stimulation. These results, then, show that in the first experiment (table 1) the thiocyanates decreased bacterial growth, and in the third experiment (table 3) they decidedly stimulated bacterial growth. Whether this stimulation is at all influenced by the calcium carbonate used in this experiment on both thiocyanate-treated and control soils, or is entirely due to the smaller amounts of thiocyanates, will have to be revealed by further experimentation.

TABLE 3

Bacterial count ($\times 100,000$) of Hempstead silt loam, 1 per cent CaCO_3 added

INCUBATION TIME	CONTROL	0.075 GM. NH_4CNS PER 100 GM. AIR-DRIED SOIL	0.075 GM. NaCNS PER 100 GM. AIR-DRIED SOIL
<i>weeks</i>			
2	88.0	207.8	183.8
6	71.7	224.0	267.0
8	131.7	243.0	279.0
10	191.0	358.6	238.7
12	129.2	302.3	206.3
14	111.4	284.0	209.5
16	63.3	289.2	152.3
18	54.7	121.5	117.5
20	65.7	146.6	136.4
22	46.8	216.4	96.6
24	42.8	167.6	156.1
26	64.8	127.5	127.9
28	51.6	129.2	121.6

After incubation, the number of algae were counted by Bristol-Roach technic (9), using the tables of probability of Halvorson and Ziegler (3, 4). Parallel with experiment 1 (table 1), where the largest quantity of thiocyanate was used, 10 replicates were made of each decimal dilution. There was neither a pronounced increase nor a decrease of algae in the treated sample. Also, by the use of Cutler's method (9) of determining total protozoa and the use of the same tables by Halvorson and Ziegler, a slightly larger number of protozoa, including cysts, were found in the treated soils than in the untreated soils. According to Halvorson and Ziegler, the differences were not significant, but the results do show that the protozoa are not decreased in such treated soils, as would be the case in a marked degree in true "partial sterilization." Later experiments will show that nitrifying bacteria were not killed, as would occur in "partial sterilization."

These experiments, then, indicate that ammonium thiocyanate increased the number of bacteria when used in amounts comparable to field practice and exerted no deleterious effect upon the soil algae and protozoa, even when used in excessively large amounts. "Partial sterilization," therefore, probably will not account for any increase in available nitrogen which the thiocyanates may cause in the soil. Any increase in ammoniacal or nitrate nitrogen must then be considered as coming from the thiocyanates added. Good growth, usually in 5 to 10 days, was found when a soil suspension was inoculated into a purely inorganic medium, with glucose as a source of energy, using distilled nitrogen-free water and sodium thiocyanate as the only source of nitrogen. These organisms were isolated by plating on the same medium agarized, and were reinoculated into the liquid medium, where heavy growth was again observed in 4 to 7 days. Thus there is no doubt that thiocyanate compounds may serve as a source of nitrogen for some organisms.

At definite periods the tumblers of Hempstead silt loam used for the bacterial counts (table 3) were emptied on clean papers, and the soil was thoroughly mixed. Ten-gram samples were used for the microbiological counts reported above. To large bottles a representative sample was added (70 gm.) in duplicate, and 140 cc. of 20 per cent sodium chloride was added. After prolonged shaking, the mixture was filtered. The treatment with sodium chloride allows the NH_4 ion to be leached out by base exchange, according to Harper (5). After filtering, a 100-cc. aliquot was analyzed for ammonia nitrogen. Nitrate nitrogen was determined in the residue by reduction with Devarda's alloy. Table 4 shows the results of these experiments.

From table 4 it will be noted that nitrification proceeded rapidly during the first few weeks of incubation. Thus it is evident that when the thiocyanates were used in amounts such as are used in practice, the nitrifying bacteria were not destroyed as in "partial sterilization." When 2 gm. rather than 0.15 gm. of the thiocyanates were added per 200 gm. of soil, nitrification was virtually stopped.

It is also evident that when ammonium thiocyanate was added to soil, only one-half of the nitrogen, on an average, was recovered as NH_3 or nitrate nitrogen, or 99.45 per cent of the nitrogen of the cation. The fluctuation of the NH_3 and nitrate nitrogen from week to week is such as is commonly found, but it seems of some significance that the fluctuations are about the 100 per cent value, the median being 100.48 per cent and the mean 99.45 per cent. The sodium thiocyanate, however, did undergo some ammonification, showing that the cyanate may become available to plants. About one-third of the N of this compound was accounted for largely as nitrates, in the latter part of the experiment, and as NH_3 in the earlier weeks. The fact that none of the anion of NH_4CNS and one third of the anion of NaCNS were accounted for as nitrate or ammoniacal nitrogen, is not surprising. Cyanates may serve as a source of N to bacteria, as was shown above, and it may also be shown that they can serve as a source of carbon, but growth is slow. When ammonium thiocyanate

TABLE 4
Nitrification in Hempstead silt loam treated with thiocyanates*

	INCUBATION TIME	NH ₃ -N PER GRAM SOIL	NO ₃ -N PER GRAM SOIL	TOTAL N (NITRATE AND AMMO- NIACAL)	TREATED TOTAL MINUS CONTROL TOTAL	PERCENTAGE AMMONIACAL N AC- COUNTED FOR	PERCENTAGE N IN NaCNS ACCOUNTED FOR
	<i>weeks</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>		
Control.....	2	0.0043	0.0920	0.0963			
NH ₄ CNS.....	2	0.1216	0.0870	0.2086	0.1123	77.50	
NaCNS.....	2	0.0170	0.0945	0.1115	0.0152		11.70
Control.....	4	0.0048	0.1150	0.1198			
NH ₄ CNS.....	4	0.0526	0.1862	0.2388	0.1190	82.13	
NaCNS.....	4	0.0124	0.1683	0.1807	0.0609		47.00
Control.....	6	0.0088	0.1218	0.1306			
NH ₄ CNS.....	6	0.0117	0.2356	0.2473	0.1167	80.54	
NaCNS.....	6	0.0124	0.1808	0.1932	0.0626		48.30
Control.....	8	0.0034	0.1297	0.1331			
NH ₄ CNS.....	8	0.0088	0.2699	0.2787	0.1456	100.48	
NaCNS.....	8	0.0114	0.1574	0.1688	0.0357		27.50
Control.....	10	0.0057	0.1246	0.1303			
NH ₄ CNS.....	10	0.0109	0.2955	0.3064	0.1761	121.53	
NaCNS.....	10	0.0091	0.1835	0.1926	0.0623		48.10
Control.....	12	0.0101	0.1300	0.1401			
NH ₄ CNS.....	12	0.0064	0.2929	0.2993	0.1592	109.87	
NaCNS.....	12	0.0064	0.1864	0.1928	0.0527		40.70
Control.....	14	0.0095	0.1287	0.1382			
NH ₄ CNS.....	14	0.0132	0.3129	0.3261	0.1879	129.68	
NaCNS.....	14	0.0131	0.1670	0.1801	0.0419		32.20
Control.....	16	0.0112	0.1295	0.1407			
NH ₄ CNS.....	16	0.0132	0.2826	0.2958	0.1551	107.04	
NaCNS.....	16	0.0125	0.1863	0.1988	0.0581		44.80
Control.....	20	0.0143	0.1368	0.1511			
NH ₄ CNS.....	20	0.0138	0.2936	0.3074	0.1563	107.87	
NaCNS.....	20	0.0102	0.1895	0.1997	0.0486		37.50
Control.....	22	0.0107	0.1373	0.1480			
NH ₄ CNS.....	22	0.0159	0.2635	0.2794	0.1314	90.68	
NaCNS.....	22	0.0237	0.1728	0.1965	0.0485		37.40
Control.....	24	0.0074	0.1284	0.1358			
NH ₄ CNS.....	24	0.0095	0.2983	0.3080	0.1722	118.84	
NaCNS.....	24	0.0129	0.1635	0.1764	0.0406		31.30

* Treatment = 0.15 gm. NH₄CNS or NaCNS per 200 gm. dry soil. NH₄CNS—theoretical amount NH₃-N added = 0.1449 mgm. per gm. soil. NaCNS—theoretical amount N added = 0.1296 mgm. per gm. soil.

TABLE 4—*Concluded*

	INCUBATION TIME	NH ₃ -N PER GRAM SOIL	NO ₃ -N PER GRAM SOIL	TOTAL N (NITRATE AND AMMO- NIACAL)	TREATED TOTAL MINUS CONTROL TOTAL	PERCENTAGE AMMONIACAL N AC- COUNTED FOR	PERCENTAGE N IN NaCNS ACCOUNTED FOR
	<i>weeks</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>		
Control.....	26	0.0177	0.1364	0.1541		100.48	43.40
NH ₄ CNS.....	26	0.0183	0.2814	0.2997	0.1456		
NaCNS.....	26	0.0157	0.1947	0.2104	0.0563		
Control.....	28	0.0082	0.1573	0.1655		93.03	32.90
NH ₄ CNS.....	28	0.0136	0.2867	0.3003	0.1348		
NaCNS.....	28	0.0169	0.1913	0.2082	0.0427		
Average NH ₃ and nitrate N recovered from cation of NH ₄ CNS.....						99.45	
Average NH ₃ and nitrate N recovered from NaCNS.....							37.10

is present, the bacteria would undoubtedly attack the more easily decomposable materials present in soil, using the ammonia necessary for metabolism. But when NaCNS is added, there would be no easily available source of N, and the thiocyanate would be attacked and NH₃ would be the by-product. When larger amounts of NaCNS were used, there was very little nitrate or ammoniacal N found in soil above that present in the control soil.

DISCUSSION

The data reveal certain facts as to the effects of thiocyanate on the soil microbial processes, although much more work is desirable on this subject. First, we can say that the algae and protozoa are not killed or reduced in number by treatment in excess of the usual field practice for weed eradication. The Rothamstad experiments have shown very definitely that when soil is subjected to the treatment known as "partial sterilization," there always results a depression in numbers so marked as to be ultimately a complete killing of algae and protozoa. These results have been confirmed a number of times (7, 10). The results here reported indicate no "partial sterilization" by thiocyanates. Even when enormous amounts of thiocyanates are incorporated in the soil, neither algae nor protozoa are killed off, nor are they reduced in number. Another result of "partial sterilization" is a sharp immediate reduction in the number of bacteria, followed by a gradual increase to numbers decidedly greater than those in untreated soil. The results here reported show a consistent and long-continued increase in bacterial population when amounts of thiocyanates such as might be used in field practice are used, and a decrease, which is maintained, when larger amounts are used. Also, it is very evident from the experiments reported that nitrifying bacteria are not killed. Nitrification proceeded promptly in all soils when treated with amounts of thiocyanates such as would be used in practice. Nitrifying bacteria are killed in

"partial sterilization." Thiocyanates, then, do not act as "partial sterilizing" agents.

The results also show that the ammoniacal nitrogen of ammonium thiocyanate can be account for largely as nitrates. This compound may be considered suitable for field and pot fertilizer trials. But the toxicity factor [which is less than that of sodium chlorate (6)] will have to be taken into consideration.

It is doubtful, however, that we can consider the CNS nitrogen directly as a very available fertilizer. Seven months after the compounds were in contact with the soil, little if any available (NH_3 and nitrate) nitrogen was found in the soil above that which could be accounted for as coming from the NH_4 radical and the soil organic nitrogen. Ammonium thiocyanate will probably be found by field trial to belong to the class of compounds which are commonly described as yielding "slowly available nitrogen." It is also indicated, but this needs confirmation, that when the "available" (nitrate and ammoniacal) nitrogen is not present, the CNS radical is indeed ammonified and nitrified, but only partially so, since, after 28 weeks, only about one-third of the nitrogen was recovered as nitrates or ammonia when NaCNS was added in amounts comparable to those of NH_4CNS that are used in field practice.

SUMMARY

When 1.25 per cent ammonium thiocyanate was added to unlimed garden soil, there was neither an increase nor a decrease in algae or protozoa.

With 1.25 per cent sodium thiocyanate or ammonium thiocyanate the number of bacteria definitely decreased in 3 and 5 weeks.

With 0.125 per cent ammonium thiocyanate there was no pronounced change in bacterial numbers in 7 weeks, but in 9 weeks there was a definite reduction.

With 0.075 per cent ammonium thiocyanate or sodium thiocyanate added to limed soil, there was always a significant increase in bacterial numbers over the control when determined at 2-week intervals up to 28 weeks.

Bacteria were isolated which grew vigorously on media the only nitrogen source of which was c.p. sodium thiocyanate.

When 1 per cent ammonium thiocyanate was added to unlimed garden soil, less than 100 per cent of the theoretical ammoniacal nitrogen could be accounted for after 2 or more weeks' incubation.

When 1 per cent sodium thiocyanate was added to unlimed garden soil, little of the theoretical thiocyanate nitrogen could be recovered as ammonia or nitrate at any time up to 7 weeks' incubation.

When 0.075 per cent ammonium thiocyanate was added to limed soil, an average of 49.7 per cent of the theoretical nitrogen (99.45 per cent of the ammonium nitrogen) was recovered in determinations every 2 weeks up to 28 weeks.

When 0.075 per cent sodium thiocyanate was added to limed soil, an average

of 37.1 per cent of the theoretical thiocyanate radical was recovered as ammonia or nitrates in determinations every 2 weeks up to 28 weeks.

Nitrification proceeded rapidly in soils treated with 0.075 per cent ammonium thiocyanate.

The application of ammonium thiocyanate in amounts used in the practice of weed eradication formed quickly available nitrogen only to one half of the nitrogen in the compound.

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EFFECT OF AMMONIUM AND NITRATE NITROGEN ON THE MINERAL COMPOSITION AND SAP CHARACTERISTICS OF BARLEY

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A previous paper (1) dealing with the ammonium and nitrate nitrogen nutrition of barley at different seasons, reported on the influence of hydrogen-ion concentration, oxygen supply, and certain metals in minute quantity on growth and development. It was found: (a) that the effect of hydrogen-ion concentration, within a physiologically tolerable range, on the growth of barley plants supplied with either ammonium or nitrate nitrogen was modified by the season of the year, and (b) that though the nitrate plants generally surpassed the ammonium plants in growth, the latter were affected extensively and favorably by either forced aeration of the culture solution or the addition of minute quantities of manganese and certain other heavy metals.

The investigation was concerned not only with the influence of the factors mentioned on the growth and development of plants as reflected in the previously reported yields (1) but also with the effects of the various treatments on the chemical composition and several characteristics of plant sap, such as conductivity, pH, and total sugars. The purpose of this paper is to present the results of these chemical studies.

METHODS AND MATERIALS

Barley plants were grown at different seasons of the year in nutrient solutions maintained within narrow limits at pH 4, 5, 6, and 6.7 respectively. A full description of the cultural methods, including the composition of the nutrient solution, was presented in an earlier article in this journal (1). Forced aeration was provided in all experiments unless otherwise indicated, by the designation "no air." The "no air" treatment in no way implies an approach to an anaerobic condition. The use of shallow tanks with loosely fitting covers permitted access of air to a large surface, providing, even in the tanks without forced aeration, an oxygen supply superior to that usually available in jars or crocks.

Each treatment was represented by 64 plants grown in the greenhouse for 5 weeks in iron tanks containing approximately 115 liters of nutrient solution.

¹ The writer gratefully acknowledges the advice received from D. R. Hoagland in the course of this investigation and wishes to thank P. R. Stout and S. B. Johnson for their assistance with part of the analytical work.

After harvest, the roots were separated from the shoots, carefully washed, and centrifuged before being weighed (9). Half of the plants from each treatment were dried at 56°C. in a ventilated oven for 72 or more hours and after being finely ground were used for total Ca, Mg, K, P, and N determinations. The remaining 32 plants were placed in tightly stoppered jars and kept in cold storage at -17° C. for later use in the determination of pH, conductivity, and total sugar concentration of the plant sap. The sap was expressed in a heavy steel screw press (9).

The following analytical methods were used:

The pH of plant sap—all pH determinations were made with the glass electrode within a few minutes after the sap was expressed.

Total sugars—the ferri-ferrocyanide method, as modified and adopted for plant materials by Hassid (5).²

Conductivity—Kohlrausch bridge equipped with a sound amplifier and ear-phones.

Potassium—volumetric cobalti-nitrite procedure of Hibbard and Stout (6).

Standard methods³ were used for the determination of calcium, magnesium, nitrogen, and phosphorus. The Kjeldahl-salicylic acid method was used to determine total nitrogen of the plants in the nitrate series; and the unmodified Kjeldahl method, of those in the ammonium series. The ammonium plants were found, by a preliminary diphenylamine test, to contain no nitrates. For phosphate determinations, the volumetric procedure involving the titration of the ammonium phosphomolybdate precipitate was used.

Manganese was determined colorimetrically as permanganate by the persulfate method. To avoid metal contamination, grinding of the dried plant material was omitted. Separate samples of several grams of dried roots and shoots were weighed, ashed, and dissolved in nitric acid, and analyses were made on suitable aliquots.

EFFECT OF SOURCE OF NITROGEN ON Ca, Mg, K, P, AND N CONTENT OF PLANTS

The results of analyses of plants grown in spring (February 28 to April 2) and in fall (October 10 to November 14) are presented in figures 1 and 2. The influence of hydrogen-ion concentration on the composition of plants supplied with either ammonium or nitrate nitrogen was tested by analyzing plants grown at pH 4, 5, 6, and 6.7 respectively. The nitrate plants were found to have a higher calcium, magnesium, and potassium, but a lower phosphorus concentration than the ammonium plants. This was the case throughout the pH range studied during both the spring and fall seasons. In fall, the nitrate plants had a higher nitrogen content than the ammonium plants, but in spring the reverse was true for plants grown at pH 6.7 and only slight differences were apparent in plants grown at pH 5 and 6. Thus, no consistent relation was found between the source of nitrogen, the reaction of the nutrient solution, and the nitrogen content of the shoots.

As for the influence of the external reaction on the absorption of anions and

² A modification of the method has been recently published by W. Z. Hassid. *Indus. and Eng. Chem., Analyt. Ed.* 9: 228-229, 1937.

³ Hibbard, P. L. 1932 Methods of chemical analysis. Department of Plant Nutrition, University of California. Mimeographed.

cations by the plant, the data presented in figures 1 and 2 do not point to any clear-cut relation. Although a trend toward increased cation nitrogen (ammonium) absorption with decreasing external hydrogen-ion concentration was found in case of the ammonium plants, such a relation was not in evidence during both seasons for the other cations: potassium, calcium, and magnesium. As for the anions, the phosphate concentration within the plant increased with an increase in the external pH; the nitrate plants however, had a higher total nitrogen content at pH 6.7 than at pH 5 in fall but not in spring.

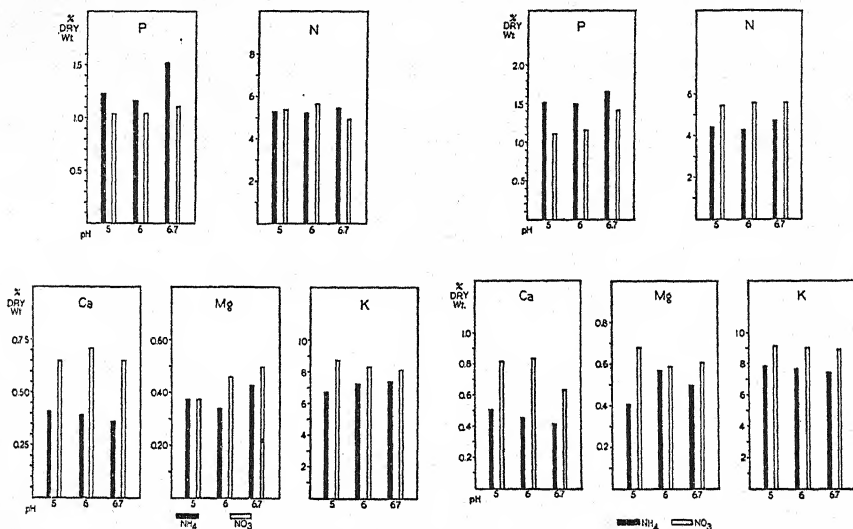


FIG. 1

FIG. 2

FIG. 1. TOTAL Ca, Mg, K, P, AND N, EXPRESSED AS PERCENTAGES OF DRY WEIGHT OF SHOOTS OF AMMONIUM AND NITRATE PLANTS GROWN IN SPRING AT VARIOUS HYDROGEN-ION CONCENTRATIONS

FIG. 2. TOTAL Ca, Mg, K, P, AND N, EXPRESSED AS PERCENTAGES OF DRY WEIGHT OF SHOOTS OF AMMONIUM AND NITRATE PLANTS GROWN IN FALL AT VARIOUS HYDROGEN-ION CONCENTRATIONS

In view of the very distinct injury observed in plants grown at pH 4 with either form of nitrogen (1), it was deemed best not to include their composition in presenting the effect of hydrogen-ion concentration on plant composition (figs. 1 and 2). The ammonium plants at pH 4 were generally characterized, however, in agreement with the foregoing observation, by a lower base and a higher phosphorous content than the nitrate plants.

The profoundly beneficial effect of aeration and manganese on the growth of ammonium plants (1) made it desirable to determine whether the intervention of these factors has altered the relative chemical composition of ammonium and nitrate plants. Plants were grown at pH 6 with and without forced aeration or added manganese (0.5 p.p.m.). The favorable effects of manganese

and aeration on the growth of ammonium plants is shown in figure 3, graph I. The dried and finely ground shoots were analyzed for total Ca, Mg, K, P, and N. The results, presented in figure 3, indicate that aeration or added manganese, which greatly improved the growth of ammonium plants, did not alter their relative chemical composition. Thus, cation nitrogen (ammonium) was found under all conditions studied, whether favorable or unfavorable for growth, to be associated with a lower base and a higher phosphorus content, whereas supplying nitrogen in the anion (nitrate) form gave a higher base and a lower phosphorus concentration in the plant. This is in agreement with the findings of Holley, Dulin, and Pickett (10) for young cotton plants.

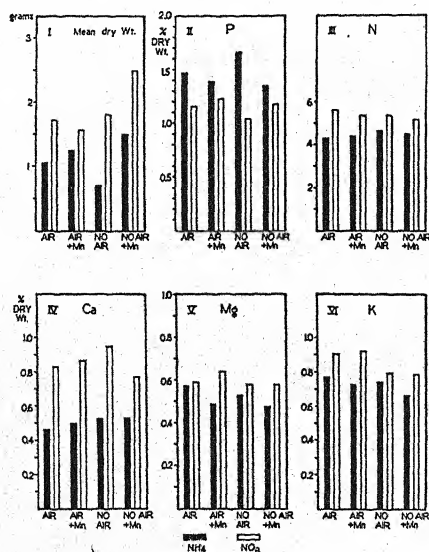


FIG. 3. EFFECT OF AERATION AND ADDITION OF MANGANESE ON GROWTH AND MINERAL COMPOSITION OF PLANTS GROWN IN FALL AT pH 6

The data presented in figures 1 and 2 describe the final composition of plants grown for an extended period and hence do not furnish direct information as to the rate of absorption of the various ions for short periods. An experimental approach to the latter problem could appropriately be made by the technic of short-time absorption experiments, using intact plants (2, 3, 14, 15), excised roots (9), or storage tissues (16).

INFLUENCE OF SOURCE OF NITROGEN ON pH, CONDUCTIVITY, AND TOTAL SUGARS OF EXPRESSED SAP

The chemical determinations on the expressed sap were carried out only on plants grown in fall. It was recognized that in expressing the sap of a root or a shoot a composite sample of several tissues is obtained and that possible alterations in one tissue resulting from an experimental treatment may be

masked by other tissues. The purpose of the following determinations was to ascertain whether, despite this difficulty of interpretation inherent in the method, some correlation existed between the several treatments and certain sap characteristics.

The pH measurements of the expressed sap are presented in table 1. The pH of the shoot sap, although somewhat lower in the ammonium than in the nitrate series, was remarkably constant except for the nitrate plants grown at pH 4, which were profoundly injured (1). In both series, the pH of the expressed root sap was found to increase slightly with increasing pH of the culture medium.

TABLE 1

Influence of external hydrogen-ion concentration on the pH of expressed sap of ammonium and nitrate plants

pH OF CULTURE SOLUTION	pH OF SAP			
	NH ₄ shoots	NO ₃ shoots	NH ₄ roots	NO ₃ roots
4	5.75	5.71	5.75	5.79
5	5.80	6.05	6.09	6.04
6	5.85	6.05	6.22	6.09
6.7	5.89	6.04	6.39	6.24

TABLE 2

Effect of aeration and added manganese on the pH of expressed sap of ammonium and nitrate plants grown at pH 6

TREATMENTS	pH OF SAP			
	NH ₄ shoots	NO ₃ shoots	NH ₄ roots	NO ₃ roots
Air.....	5.85	6.05	6.22	6.09
Air + Mn.....	5.73	6.00	6.08	6.04
No air.....	5.85	5.86	6.20	6.21
No air + Mn.....	5.77	5.87	6.08	6.08

The data presented in table 2 indicate that neither aeration nor the addition of manganese materially affected the reaction of the expressed sap of plants grown at pH 6. The significance of such small fluctuations as were noted—the lowering of the pH of the sap of ammonium plants with the addition of manganese, and the increase in the pH of the sap of nitrate plants with forced aeration—cannot be evaluated on the basis of information now available. In general the pH of the sap was found to be only slightly affected by the external hydrogen-ion concentration and by such factors as aeration and the addition of manganese. The relative constancy of the pH of sap extracted from plants grown under varied conditions is regarded as warranting emphasis.

A notable distinction between the chemical characteristics of ammonium and nitrate plants was found in determining the conductivity of the expressed

plant sap. The root sap of ammonium plants had a consistently lower conductivity than that of the nitrate plants, as shown in figures 4 and 5. The relative difference in conductivity occurred, similarly to the previously discussed differences in mineral composition, under all the experimental conditions investigated. This marked distinction between the ammonium and nitrate plants in the conductivity of expressed sap was manifest in the roots; the conductivity of the shoot sap showed relatively small fluctuations in the two series, but it was again higher in the nitrate shoots. Since the conductivity of plant saps may be affected by a number of factors other than ionic concentrations (4), the consistently higher conductivity of the root sap of nitrate as compared with ammonium plants (twice as high in many instances) would seem to justify a detailed study of the individual ionic concentrations as well as other chemical

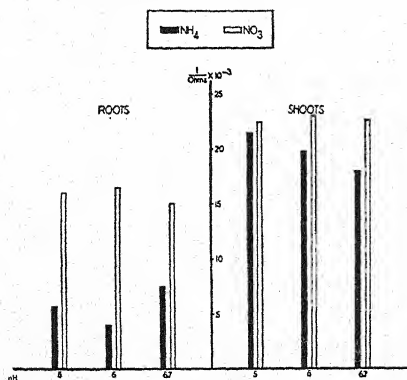


FIG. 4

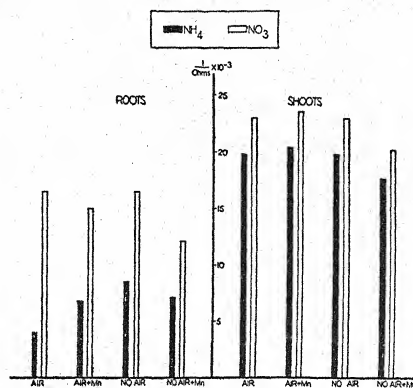


FIG. 5

FIG. 4. CONDUCTIVITY OF THE EXPRESSED SAP OF AMMONIUM AND NITRATE PLANTS GROWN IN FALL AT VARIOUS HYDROGEN-ION CONCENTRATIONS

FIG. 5. EFFECT OF AERATION AND THE ADDITION OF MANGANESE ON THE CONDUCTIVITY OF THE EXPRESSED SAP OF AMMONIUM AND NITRATE PLANTS GROWN IN FALL AT pH 6

properties of the root saps from these two different sources—an undertaking which exceeded the scope of the present investigation.

Another distinction between the ammonium and nitrate plants was found in the concentration of total sugars in the expressed sap of shoots. The ammonium plants had, under the conditions investigated, a higher sugar concentration than the nitrate plants (fig. 6). This is in agreement with the findings of Holley, Dulin and Pickett (11). Within the ammonium series, plants grown at pH 6 had a higher sugar content than those grown at any other pH value, whereas the nitrate plants showed little variation with pH.

An interesting relation between manganese and total sugar concentration was noted. The addition of manganese to the nonaerated ammonium and nitrate nutrient solutions was associated with a marked increase in the sugar concentration of the sap (fig. 6) and accompanied improved growth in both

cases (fig. 3). In the aerated cultures, however, the addition of manganese brought about a decrease in the sugar concentration, coincident with a depression in growth of the nitrate plants, but not of ammonium plants. The possible relation of manganese to carbohydrate metabolism in higher plants is now being investigated in this laboratory.

In view of the restricted growth made by the ammonium plants, it is questionable whether the higher sugar concentration found in the sap may be regarded as an indication of favorable metabolic activity. The concentration of sugars in the sap is at any given time an index not only of synthesis but also of carbohydrate utilization by the plant. A high sugar content may thus result from the absence of favorable conditions for its utilization.

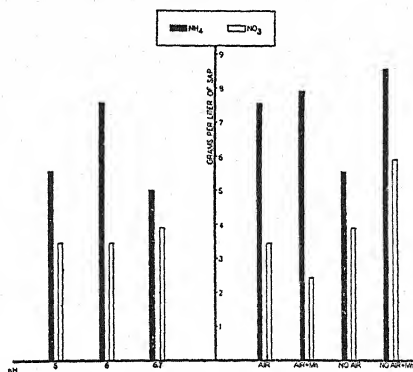


FIG. 6. TOTAL SUGARS IN THE EXPRESSED SAP OF SHOOTS OF AMMONIUM AND NITRATE PLANTS GROWN IN FALL

Left—effect of hydrogen-ion concentration.

Right—effect of aeration and the addition of manganese on plants grown at pH 6.

INFLUENCE OF AMMONIUM AND NITRATE NITROGEN ON MANGANESE CONTENT OF PLANTS

The very favorable effect of manganese on the growth of barley plants supplied with ammonium nitrogen as the sole source of nitrogen suggested a relation between the source of nitrogen and manganese nutrition. A special experiment set up at a later season to provide material for manganese analyses afforded an additional opportunity to confirm the favorable effect of aeration and manganese on the utilization of ammonium nitrogen by barley plants. Chemical analysis disclosed striking differences in the manganese content of the roots of ammonium and nitrate plants (table 3).

In every case, the roots of nitrate plants were found to contain several times as much manganese as the roots of ammonium plants. The addition of manganese to the nutrient solution (0.5 p.p.m.) brought about an enormous increase (fifty to a hundred fold) in the manganese content of the roots; but again, the nitrate plants absorbed several times as much manganese as the ammonium plants. Aeration (cf. series 2 and 4) favored the absorption of

manganese—a fact particularly marked in the case of ammonium plants, for which the manganese concentration in the aerated roots was about three times as high as that in the unaerated roots.

In contrast with the roots, the shoots of ammonium and nitrate plants, on analysis, revealed no great differences in manganese content. In the plus manganese cultures (series 2 and 4), the nitrate shoots had a higher manganese content than the ammonium shoots. In nutrient solutions without added manganese (series 1 and 3) the manganese content of the shoots of both ammonium and nitrate plants is virtually the same, except for the ammonium shoots in the unaerated cultures (series 1). Aeration increased the manganese content of ammonium shoots (series 3) to a level comparable with that of the nitrate plants, but did not alter the manganese content of the latter. As the nitrate plants also made more growth than the ammonium plants, the higher manganese content of the former is even more impressive when expressed as an amount in a plant rather than on a concentration basis.

TABLE 3
Manganese content of ammonium and nitrate plants
In p.p.m. of dry weight

SERIES	TREATMENT	NH ₄ ROOTS	NO ₃ ROOTS	NH ₄ SHOOTS	NO ₃ SHOOTS
1	No air	<3	14.5	<1	10.4
2	No air + Mn	151	1070	47.6	78.0
3	Air	<5	17.1	11.6	10.8
4	Air + Mn	540	1330	75.0	90.3

The data presented in table 3 further indicate that, although the manganese concentration of barley roots can be increased as much as a hundred fold by adding manganese to the nutrient solution (cf. series 3 and 4), it is subject to less variation in the shoots; but a high manganese concentration in the roots is associated with an increased concentration in the shoots.

The higher manganese content of nitrate roots in the minus-manganese cultures (series 1 and 3) might conceivably be attributed to greater impurities of this element in the nitrate nutrient solutions. Although no purification procedures were used in the present experiments, this possibility is considered unlikely, because of other experiments with purified nutrient salts, in which the differential responses of ammonium and nitrate plants to aeration and manganese likewise occurred (1).

DISCUSSION

The chemical investigations of barley plants reported in this paper were undertaken in order to determine whether the differential response to ammonium and nitrate nitrogen can be correlated with some modification in the chemical composition of the plant which could serve as a basis for explaining the

effect of these two sources of nitrogen on the growing plant. It was sought to ascertain, on one hand, whether some consistent modification in the mineral composition and sap characteristics can be associated with the generally poorer growth obtained with ammonium nitrogen than with nitrate nitrogen, and on the other hand, whether the observed large and favorable effect of aeration and the addition of microelements, particularly manganese, had its counterpart in some chemical change within the plant.

The presented data, referring only to several constituents of one plant species, cannot of course, by themselves serve as a basis for valid generalizations. Certain general relationships found to occur with consistency may, however, be stressed. Ammonium plants had a lower base content [cf. review by Nightingale (13)] and a higher phosphate content than nitrate plants. This, pointing to a relationship between the ionic form of nitrogen and the absorption of other ions from the culture solution, was found to hold throughout the pH range investigated, with or without forced aeration or added manganese, which favorably affected the growth of ammonium plants. It does not seem likely therefore, that this relative alteration in the mineral composition as a concomitant of ammonium absorption constitutes a necessarily unfavorable adjustment on the part of the plant. Similarly, the lower conductivity of root sap and the higher sugar content of the shoot sap of ammonium plants were found to persist even when growth was favorably influenced by forced aeration and the addition of manganese.

The manganese analyses, however, indicate a possible correlation between the absorption of this element and the differential response to the two forms of nitrogen. Nitrate plants—roots in particular—were characterized by a higher manganese content than that of ammonium plants. What is suggestive, however, is that improved growth of ammonium plants was associated with an increased manganese content; thus, both forced aeration and the addition of manganese resulted in an increased manganese content of the ammonium plant.

The question arises whether the beneficial effect of aeration on the growth of these plants may be ascribed, in part at least, to bringing about more effective absorption of such metallic microelements as manganese. This function of aeration may be of considerable importance to ammonium plants when, as in the present experiments (table 3, series 1 and 3), the manganese concentration was necessarily very small, being accounted for solely by incidental contamination of the C. P. chemicals and the distilled water used. In the absence of forced aeration, increased manganese absorption by ammonium plants, coincident with improved growth, was brought about by adding manganese to the nutrient solution.

The possibility that some manganese was either adsorbed or precipitated on the surface of the roots may raise the question whether the reported values reflect the actual concentration of manganese within the roots. Regardless of its distribution, however, the consistent difference in manganese content between the nitrate and ammonium roots is regarded as significant.

The presented data support the earlier expressed view that nitrate nitrogen may be of value to the plant in addition to serving as a source of nitrogen (1). In the present instance nitrate was found to be associated with a higher manganese content than ammonium nitrogen, particularly in the roots. This experimental finding may be explained by the stimulative effect of nitrate nitrogen on root respiration in its relation to mineral absorption [cf. discussion in (1)] or by such ionic interrelationships as are to be discussed presently, or by both.

Since different species of plants vary greatly in their requirements with respect to aeration and manganese supply, it is not to be expected that the relation of these factors to nitrogen nutrition, as reported for barley, will be encountered without modification in other plants. Tomato plants for example, as contrasted with barley, require a relatively high manganese and a liberal oxygen supply with either nitrate or ammonium nitrogen. Experiments now in progress are concerned with the relation of aeration and manganese supply to the utilization of ammonium and nitrate nitrogen in plants other than barley.

The ionic form of nitrogen in the culture solution assumes great importance in view of the very large amounts of this element used by the plant and the rapid rate of absorption of both ammonium and nitrate ions. If ammonium instead of nitrate is used as the sole source of nitrogen in the nutrient solution, a rapidly absorbable cation is substituted for a rapidly absorbable anion. The rates of absorption of phosphate and sulfate ions, the only other anions present in the ammonium nutrient solution, (except ions, such as bicarbonate, derived from the plant) are very slow (7).⁴ Thus the ammonium nutrient solutions contain two rapidly absorbable cations (NH_4^+ and K^+) but no rapidly absorbable anions, whereas the nitrate nutrient solutions contain a pair of rapidly absorbable ions of opposite charge (K^+ and NO_3^-).

Although, as already pointed out, the data presented pertain to the final composition of plants grown for an extended period and hence do not furnish direct information as to the mechanism of mineral absorption, they nevertheless lend support to the view that one ion influences the absorption of another (7, 12). The lower cation and higher anion content of ammonium plants (table 4) can be attributed to such interionic effects, if it is assumed that at least part of the nitrogen is absorbed as NH_4^+ . The rapid absorption of this cation would tend to depress the absorption of other cations and to increase the absorption of anions. Conversely, the rapid absorption of nitrate ion by nitrate plants would tend to depress the absorption of other anions such as phosphate, and to increase the absorption of the cations, calcium, magnesium, and potassium.

These relationships are brought out in table 4, in which the cations and

⁴ Hoagland, D. R., and Broyer, T. C. Unpublished data.

anions removed by plants from the culture solution have been computed. (It is not implied, of course, that all the absorbed ions remain as ions within the plant). The phosphate was considered to have been absorbed as H_2PO_4^- , since this is the predominating ion throughout the pH range studied. In the ammonium plants the total nitrogen has been included in the cation fraction; and in the nitrate plants, in the anion fraction. No sulfate determinations were made, but, considering the relatively low amounts of sulfate usually found in barley plants, it appears almost certain that the inclusion of sulfates in the anion fraction would leave the relation of anions to cations, as presented in table 4, essentially unaltered.

In the ammonium plants there is a great preponderance of absorbed cations over anions. Within the plant, the electrostatic balance among the ions unincorporated in organic substances is maintained by the production of organic acid anions. In the nutrient solution, however, the excessive removal of cations is accompanied by an increase in the hydrogen-ion concentration and

TABLE 4
Total cations and anions of the shoots of ammonium and nitrate plants grown in fall
In m.e. in 100 gm. dried tissue

pH OF CULTURE SOLUTION	NH ₄ SHOOTS		NO ₃ SHOOTS	
	Total cations	Total anions	Total cations	Total anions
5	576	48.8	331	439
6	574	47.4	321	437
6.7	592	52.6	311	436

accounts for the well-known physiological acidity of nutrient media provided with ammonium salts as the sole source of nitrogen. [It is not implied, however, that ammonium nitrogen is absorbed exclusively as NH_4^+ . The view that it may be absorbed, at a suitable pH, as an undissociated molecule of NH_4OH or NH_3 meets with little opposition from the adherents of the ionic conception of mineral absorption (8).]

In the nitrate plants there is, in agreement with the results of McCalla and Woodford (12), a preponderance of absorption of anions over cations, accounted for by the large absorption of nitrate nitrogen. The removal of anions in excess of cations from the nutrient solution is balanced mainly by the bicarbonate ion, derived from the plant. As suggested by Hoagland and Broyer (9), the effect is that of an exchange of bicarbonate for nitrate ion. The well-known tendency of most plants grown in acid nutrient solutions, supplied with nitrate salts as the sole source of nitrogen, to shift the external reaction toward neutrality, can be explained by the exchange of nitrate, the anion of a strong acid, for bicarbonate, the anion of a weak acid.

As for the oft discussed relation between the external hydrogen-ion concen-

tration and the absorption of cations and anions by the plant,⁵ the data presented do not warrant any attempt at generalization. The absence of a consistent relationship during the two seasons of the year, between the external hydrogen-ion concentration and the absorption of the several cations, as one group, and the anions, as another, is in agreement with the view that there is little to be gained in attempting to interpret the effects of the external reaction in terms of a single variable, apart from other factors influencing the growth and metabolism of plants (1, 8, 9).

SUMMARY

Calcium, magnesium, potassium, nitrogen, and phosphorus analyses as well as determinations of pH, conductivity, and total sugars of the expressed plant sap were made on 5-week-old barley plants grown in nutrient solutions supplied with either ammonium or nitrate as the sole source of nitrogen.

The plants were grown at different seasons with control of the variables of hydrogen-ion concentration, aeration, and concentration of manganese.

Ammonium plants had, under all conditions tested, a higher phosphorus and a lower calcium, magnesium, and potassium content than nitrate plants. No consistent relation was found between the source of nitrogen, the external reaction, and the nitrogen content of the plant.

No consistent relation was found for the two seasons of the year, between the reaction of the nutrient solution and the absorption of cations versus anions.

Varying the pH of the nutrient solution within a range from pH 4 to pH 6.7 had little influence on the pH of the expressed plant sap, which remained unaltered within narrow limits.

The sap of shoots of ammonium plants had a consistently higher sugar concentration than that of nitrate plants.

The root sap of ammonium plants had a very much lower conductivity, under all conditions investigated, than the root sap of nitrate plants; the conductivity of the shoot sap varied but little between ammonium and nitrate plants.

Nitrate plants had a greater absorptive power for manganese than did ammonium plants. The possible relation of limited manganese absorption to the restriction of growth of ammonium plants is discussed.

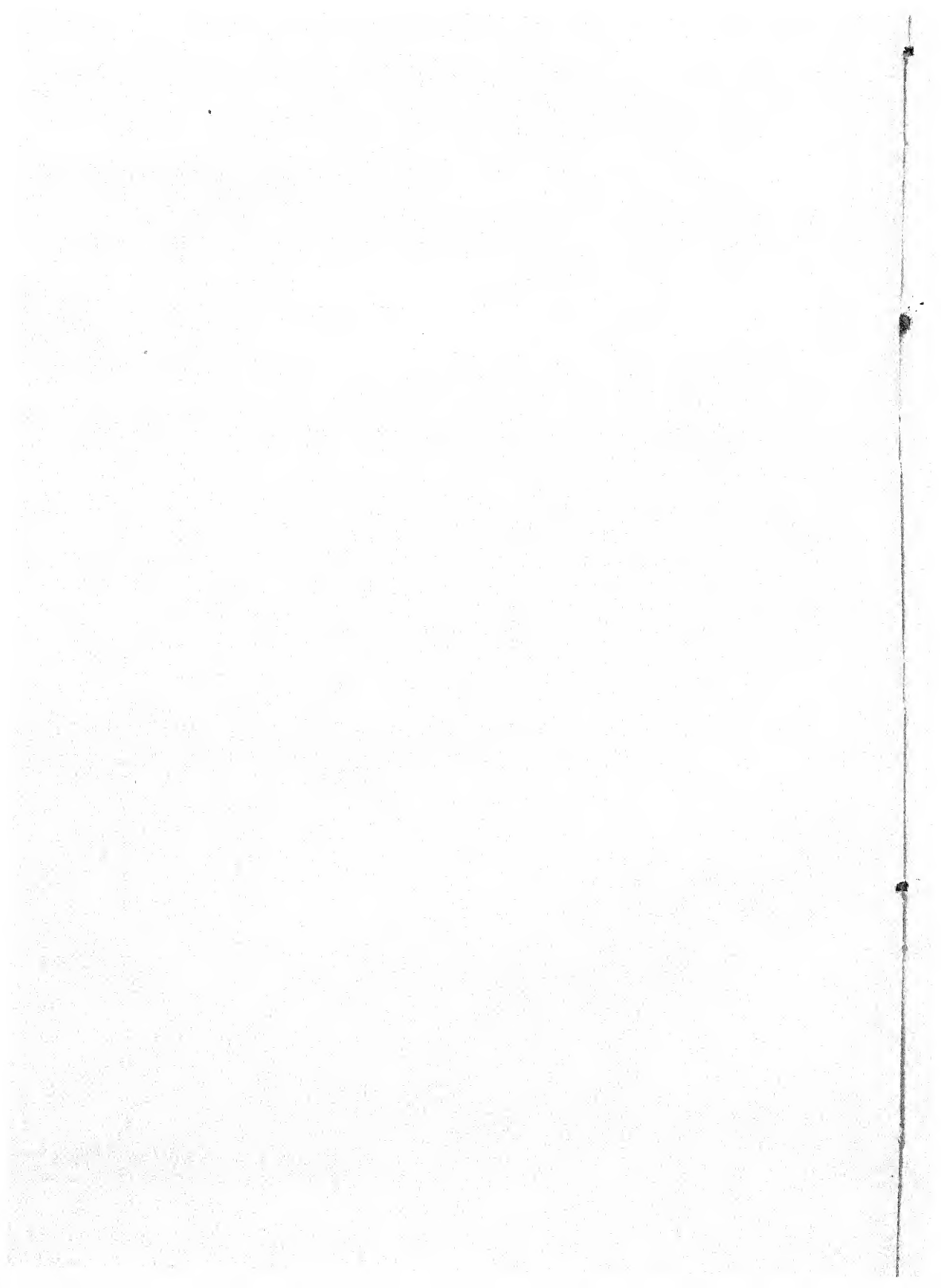
The influence of the ionic form of nitrogen on the absorption of other ions is discussed.

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ABSORPTION OF IRON FROM FINELY GROUND MAGNETITE BY CITRUS SEEDLINGS¹

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In connection with extensive sand culture studies, Eaton (3) found that finely ground magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) incorporated with the sand served as an excellent source of iron. These findings have been confirmed, and in the course of several years' work on problems of citrus nutrition some incidental results of interest bearing on both the iron nutrition of plants under alkaline soil conditions and the root-soil particle mechanism of nutrient absorption have been obtained. It is the purpose of this paper to describe briefly these observations.

The local zone or root-soil particle interface feeding of plants in soils is a concept commonly held among students of soil-plant interrelations. The work of older plant physiologists demonstrating the etching action of plant roots on various acid-soluble substances (2), the investigations of Parker and his co-workers (5) on phosphate nutrition, and, more recently, the studies of Jenny and Overstreet (4) on exchange absorption from clay suspensions by barley roots are but a few of the observations which indicate the probable existence of some sort of interfacial or contact feeding.

The very low solubility of magnetite in neutral or slightly acid solutions implies, as suggested by Eaton (3), that the ability of plants to obtain adequate iron from this source must depend upon the formation of intimate contacts between the root and the iron oxide particles in which conditions for the solution or extraction of iron must differ from those prevailing in the external nutrient solution.

EXPERIMENTAL

Confirmation of this inference was obtained in connection with an experiment originally set up to determine whether the traces of iron naturally present in a certain quartz sand were available for citrus seedlings.

In this experiment (subsequently referred to as experiment 1), three 2-gallon earthenware pots were filled with the quartz sand in question. Finely ground magnetite (particle sizes roughly 1μ in diameter) at the rate of 0.1 gm. per 100 gm. of quartz sand was incorporated into two of the pots; the third was untreated. The three pots into which citrus seedlings were transplanted were periodically flushed with an iron-free nutrient solution from a common reservoir,

¹ Paper No. 400, University of California Citrus Experiment Station, Riverside, California.

the solution displaced from each pot at the time of flushing flowing back by gravity into the common reservoir. The sand cultures were flooded at hourly intervals during daylight, a time-clock controlled air-ejector pumping mechanism (1) being used to pump the solution from the reservoir to the surface of the sand cultures. Changes in the nutrient solution, due to absorption of nutrients and water, were compensated for by appropriate additions as needed, and the reaction was maintained at values fluctuating between pH 5.8 and 7.0. The solutions were completely renewed at monthly intervals.

Early in the experiment the citrus seedlings in the pot containing no magnetite developed iron chlorosis and made no further growth, whereas the plants in those pots containing magnetite showed no evidence of chlorosis and continued to grow normally. This experiment was continued for over a year, during which time the "no magnetite" plants remained alive but failed to make any growth. The relative growths made in the three pots during this period are depicted in plate 1, figure 1. Since the circulating nutrient solution passed repeatedly through the pots containing the magnetite, it is apparent that not enough iron was brought into solution, at the pH values maintained, to meet the iron requirement of the plants in the pot containing no magnetite. It is equally evident that the plant roots in the pots containing magnetite must have made intimate contact with the iron particles and developed local feeding zones.

To determine the solubility of magnetite at acidities which might conceivably develop in such zones, CO₂-free air and CO₂ gas, respectively, were bubbled through suspensions of (a) magnetite and water and (b) magnetite, calcium carbonate, and water. These suspensions were then rapidly filtered, pH determinations being made with the glass electrode just prior to filtering. Colorimetric iron determinations were made on 50-ml. aliquots of the filtrate. The results obtained (table 1) show, as was expected, that the solubility of the magnetite definitely increases with increasing H-ion concentration. This suggests that the CO₂ excreted by plant roots creates in those local zones of contact between root and iron particles a degree of acidity exceeding that of the solution external thereto and sufficient to dissolve enough iron for plant needs.

Although the foregoing evidence leaves little doubt as to local zone feeding on the magnetite particles, further observations indicate that the ability of plants to obtain adequate iron from a given quantity of this oxide is influenced by various conditions in the external nutrient medium. In a test with sand cultures containing 0.1 per cent magnetite, the addition of 2.5 per cent precipitated calcium carbonate (thoroughly mixed with the sand and magnetite) brought about iron chlorosis in citrus seedlings. The addition of more magnetite (the plants having been temporarily removed to permit the magnetite addition) made it possible for the plant again to obtain adequate iron. In order to confirm these results, this experiment was repeated.

In this latter experiment, one pot was treated first with magnetite at the

rate of 0.5 per cent, the iron oxide being thoroughly mixed with the sand. Calcium carbonate at the rate of 2.5 per cent was then added. Two other pots were treated with 0.1 per cent magnetite and 2.5 per cent calcium carbonate; in one the iron oxide being added first, in the other the calcium carbonate added first. Small sweet orange seedlings selected for uniformity were transplanted into the jars.

The cultures were flushed with nutrient solution from a common reservoir, the technic in all particulars being identical to that of experiment 1, save that no adjustments of pH were made. The results of this experiment were in complete agreement with the aforementioned tests. A picture taken during the early stages of this latter experiment showing the iron chlorosis of sweet orange seedlings in pots containing 0.1 per cent magnetite as contrasted with the normal growth in the other pot containing 0.5 per cent magnetite is shown in plate 1, figure 2.

TABLE 1
Solubility of magnetite at various pH values

NATURE OF SUSPENSION AND TREATMENT	pH OF SUSPENSION	Fe IN FILTRATE
		<i>p.p.m.</i>
0.1 gm. magnetite, 2.5 gm. CaCO ₃ , 100 ml. distilled water through which CO ₂ -free air passed.....	8.21	< .005*
0.1 gm. magnetite, 2.5 gm. CaCO ₃ , 100 ml. distilled water through which CO ₂ gas passed.....	5.90	.010
0.1 gm. magnetite, 100 ml. distilled water, through which CO ₂ gas passed.....	4.10	.500

* Not enough iron present in 50 ml. filtrate for determination. It is possible to detect as little as 0.00025 mgm. Fe in 50 ml., hence the amount present in this case must have been less than 0.005 p.p.m.

The iron chlorosis brought about by the addition of CaCO₃ is probably the result of the increased alkalinity of the system, and the diluting effect of the calcium carbonate. The size of the calcium carbonate particles, as examined under the microscope, was of about the same order of magnitude as that of the iron oxide particles and would diminish the total exposed surface of the magnetite by partially covering their surface.

Since it was found that by adding more magnetite to the sand the effects of the calcium carbonate were overcome, the alkalinity of the system being unchanged, it might be supposed that the diluting effect was wholly responsible for the development of chlorosis. This does not necessarily follow, however, for a decrease in solubility of the iron in the contact zones might be compensated by an increased number of contacts.

It does seem certain, from these experiments, that the iron chlorosis brought on by the addition of CaCO₃ with its effect on the alkalinity of the system is due to reactions or effects external to the plant root rather than to decreased

availability or immobility of the iron inside the plant; it would be difficult to explain the curative effect of increasing magnetite (the alkalinity of the system being unchanged) if inactivation of iron within the plant were the proper explanation.

That iron solubility in the contact zones is influenced by changes in the pH of the external nutrient solution is indicated by another observation made in connection with this experiment. During the course of this test, the hourly flushing of the cultures was discontinued for about 10 days while some changes in the compressed air line were being made. Curiously enough, the iron chlorotic plants in the low-magnetite pots began to recover from their chlorosis. When the hourly flushing was resumed, the plants again became chlorotic. This effect of frequent versus infrequent flooding periods was checked repeatedly, the results obtained every time being the same.

In testing the pH of the nutrient solutions under the influence of frequent versus infrequent flooding, it was invariably found that higher values prevailed with frequent flushing. Determinations of the pH of the nutrient solution draining out of the jars after continuous circulation for a 48-hour period through the sand cultures containing calcium carbonate gave values of 8.2. On the other hand, with periodic flushing at hourly intervals during daylight, the reaction of the selfsame nutrient solution dropped to values ranging from 7.3 to 7.5. With even less frequent flushing, the values dropped lower.² Apparently, with infrequent circulation, the carbonic acid resulting from root respiration reacts in part with calcium carbonate to form calcium bicarbonate and also accumulates to some degree as carbonic acid, causing the pH value of the entire culture solution to drop to about 7.0. With frequent circulation, on the other hand, the aeration of the solution incident to pumping decreases carbonic acid accumulation, and the pH value increases. Under the latter condition iron chlorosis develops because of the inability of the plant roots to develop enough sufficiently acid contact zones for the solution of adequate iron. The rapid removal of the CO_2 or H_2CO_3 , incident to frequent flooding, which, under conditions of infrequent flushing must of necessity be higher in those somewhat vaguely defined zones surrounding the roots, would create a pH gradient between the contact zones and the external solution conducive to more rapid diffusion between these zones. These observations indicate that the contact areas between roots and soil particles, while in some measure independent, are not wholly so.

CONCLUSIONS

It was shown that the absorption of iron from finely ground magnetite, used as a source of iron in sand cultures for citrus seedlings, is made possible by the formation of intimate contacts between root and iron oxide particles in which conditions for the extraction or solution of iron must of necessity be different from those prevailing in the nutrient solution external thereto.

² The reaction of CaCO_3 suspensions through which CO_2 is being continuously bubbled will reach values as low as pH 5.6.

With an amount of magnetite sufficient under ordinary conditions (0.1 per cent), the addition of calcium carbonate brought about iron deficiency; however, with an increased amount of magnetite, the plants were again able to obtain adequate iron despite the presence of calcium carbonate. It was also found that in CaCO_3 cultures containing 0.1 per cent magnetite, less frequent flooding enabled the plant to obtain adequate iron, whereas frequent flooding brought on iron chlorosis. This was shown to result from pH differences developing under the variable flushing frequency technic.

The foregoing results emphasize the view that the "soil solution" consists of separate, though not altogether independent parts; one, and perhaps the most heterogeneous, those intimate contact zones between roots and all manner of soil particles; the other, the solution external thereto. Under conditions of ample moisture supply, these two phases are, to some extent at least, intercommunicating, and, by virtue of diffusion, capable of exerting mutual influences one on the other. The contacts between root surface and soil particle may exist in all degrees of intimacy, and in some, as postulated by Jenny and Overstreet (4), there may be no true solution phase, in the sense that the ions are not able to diffuse freely, being bound by the electrical forces existing at the root and soil particle surfaces.

It is probable that the number as well as the intimacy and character of the contacts is important in determining the final question of nutrient adequacy or inadequacy.

The observations reported suggest that the ability of plants to obtain adequate iron from alkaline soils is in part due to contact feeding on iron-bearing minerals. The occurrence of iron chlorosis in some calcareous soils and not in others may, in some cases, be due to differences in the amount of potentially available iron compounds present.

Under the influence of irrigation it is a common observation that iron chlorosis often develops. This may be, in part, the result of a gradual coating over of iron minerals with insoluble carbonates, the latter derived, of course, from the bicarbonate present in most irrigation waters. Increasing pH, also a result of this slow deposition of carbonate, is probably involved as well.

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PLATE 1

EFFECT OF MAGNETITE ON GROWTH OF SWEET ORANGE SEEDLINGS IN SAND CULTURES

FIG. 1. Growth of seedlings in sand cultures with and without magnetite: A, no magnetite; B and C, 0.1 per cent magnetite incorporated in sand.

FIG. 2. Growth of seedlings in sand cultures containing 2.5 per cent calcium carbonate with 0.1 and 0.5 per cent magnetite: A, green vigorously growing plants in pots containing 0.5 per cent magnetite; B and C, iron chlorotic plants in pots containing 0.1 per cent magnetite.

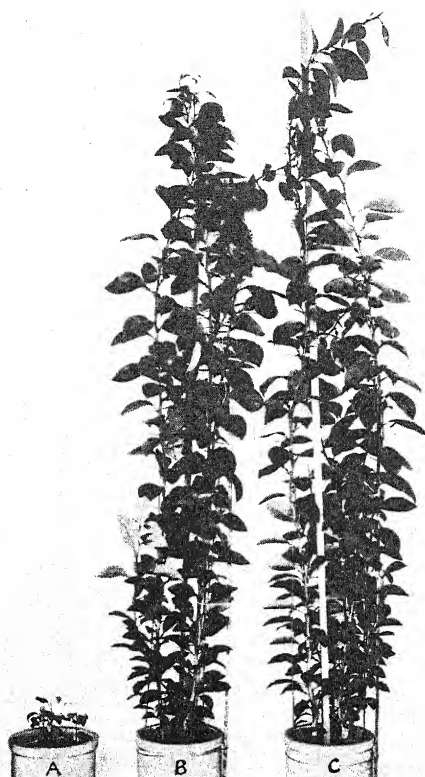


FIG. 1

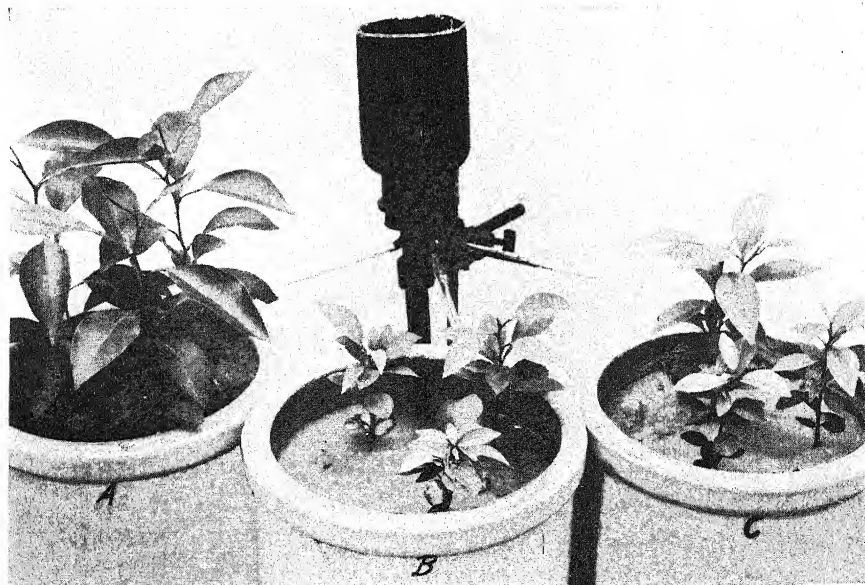


FIG. 2

SUMMARY OF RECENT INVESTIGATIONS ON BRAZILIAN SOILS

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The following is a summary of investigations recently conducted by the author in his studies on Brazilian tropical lateritic soils and semiarid soils from northeastern Brazil.

THE ALCOXIC INDEX

It is difficult to predict the fertility of lateritic soils on the basis of ordinary types of laboratory study. Their base-exchange capacity is usually very low (0-1 m.e. per 100 gm.), and there appears to be no direct relation between base-exchange capacity of these soils and fertility. The total acid property of these soils, however, is related to fertility. An attempt has been made, therefore, to find a measure of their total acid property, which should include replaceable H ions, free acids, surface absorptive power, and amphoteric compounds. The best results were obtained by titrating a given amount of soil with alcoholic 0.1N NaOH. This can be done quickly and easily by the following method: Vigorously shake 5 gm. of air-dried soil with 50-100 cc. of alcoholic 0.1N NaOH, in a small stoppered flask. After settling 5 to 10 minutes, an aliquot of the supernatant solution is drawn off with a pipette and titrated with 0.1N HCl, brom thymol blue being used as indicator. The result, expressed as cubic centimeters of NaOH neutralized per 100 gm. soil, is designated the "alcoxic index." It has been found that all the tropical lateritic soils studied gave alcoxic indexes proportionate to their fertility, the more fertile soils giving indexes ranging from 400 to 800.

The relation between alcoxic index, fertility, and Hissink's *S* value are shown by the following example:

Horizon	Alcoxic index	<i>S</i> values
A	500	0.5
B	300	2.0
C	150	6.0

It is reasonable to assume that each horizon of the soil is in equilibrium with that immediately in contact with it. The supposition is logical, therefore, that as plants absorb bases from the A horizon, the bases immediately below tend to move upward. Hence, a continuous supply of bases is furnished by the deeper-lying horizons of the profile. Obviously, not all soils are characterized by such a regular increase in *S* value with depth, or by a regularly de-

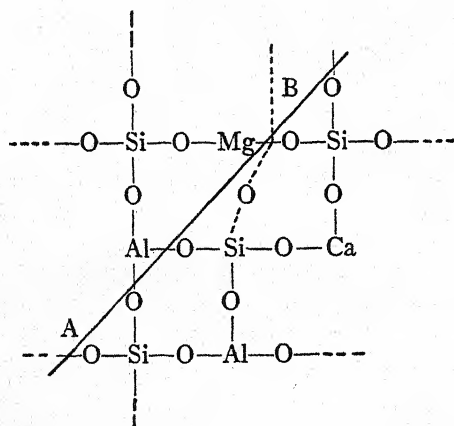
creasing alcoxix index. In fact, different tropical soils vary substantially in this respect.

The following factors influence the alcoxix index:

1. Organic matter greatly increases the alcoxix index, and the same effect is produced by grinding the soil.
2. $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Ti}(\text{OH})_4$, and SiO_2 increase the alcoxix index.
3. Heating to 600°C . has no effect except with soils high in humus.
4. The alcoxix index is diminished by heating the soil to 800°C . or higher.

That organic matter should increase the alcoxix index is logical because humus and cellulose react like the zeolites with reference to exchange of cations.

The increase in alcoxix index produced by grinding is comparable to that produced on the base-exchange capacity, as found by Kelley and Jenny.¹ This increase in alcoxix index is related to the effect on base-exchange capacity probably for the following reasons:



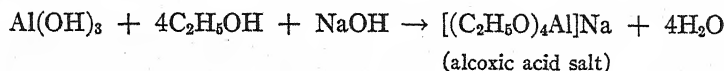
When the crystal is broken along the line A-B, the increase in base-exchange capacity is determined by the exposure of Mg, whereas the increase in H values is caused by the exposed O's which are left attached to Si. In the unbroken crystal these valences are both protected and satisfied by the adjacent oppositely charged ions.

With certain compounds grinding changes neither the base-exchange capacity nor the alcoxix index. The heteropolar constitution is altered, however, in such materials as lignin, starch, gums, and resins.

The increase in alcoxix index produced by adding $\text{Al}(\text{OH})_3$ and other amphoteric substances is due to the formation of insoluble Na salts in the alcoholic alkaline solution. It is interesting to note that $\text{Al}(\text{OH})_3$ acts as a monovalent

¹ Kelley, W. P., and Jenny, H. 1936 The relation of crystal structures to base exchange and its bearing on base exchange in soils. *Soil Sci.* 41: 367-382.

radical in an alcoholic solution of NaOH and can be titrated as shown by the following equation:



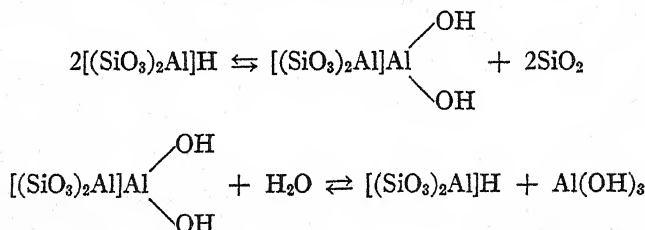
The modification of the alcoic index by heating complex silicates to 800° C. is due to the formation of the macromolecular structure. Likewise, it is interesting to note that high temperature destroys the molecular structure of organic substances and thus lowers their alcoic indexes.

ALKALI SOILS OF SEMIARID NORTHEASTERN BRAZIL

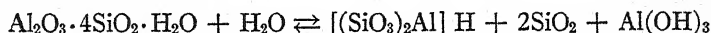
Acid lateritization and alkali lateritization

In various Brazilian publications² the author has presented his explanation of laterite and alkali soil formation. The relation of these two types of soil formation is illustrated by the following reactions:

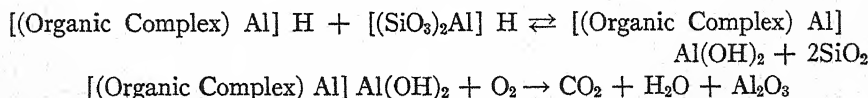
Mineral lateritization



The latter reaction is similar to the hydrolysis of montmorillonite:

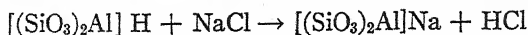


Organic lateritization

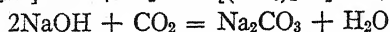
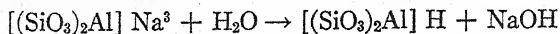
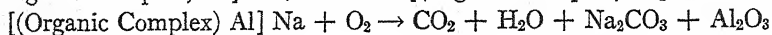
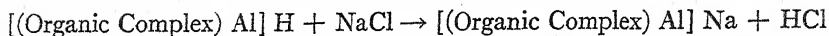


In tropical humid climates, the instability of the free and the acid zeolitic compounds leads to the first step in laterite formation. The completion of the process involves the oxidation of the complex organic aluminum ion and other base combinations.

² Barreto, A. 1937-38 *Rev. Agr., S. Paulo, Brazil*; Barreto, A. 1938 *Boletim das Obras Contra as Secas*.

Mineral alkali formation in the presence of organic matter

In dry climates the HCl volatilizes.

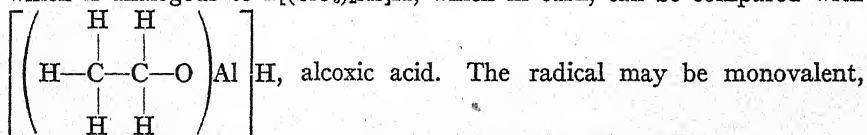
*Organic-alkali lateritization*

These reactions can be produced in the laboratory, for example, by adding a solution of NaCl to an organic soil and evaporating to dryness several times, and also by oxidizing a mixture of organic soil and NaCl at 500°C.

In Brazil we find that many alkali soils give a very low alcoxix index. These soils are considered to have a very low fertility value even if freed from their alkali properties. Certain Brazilian alkali soils, relatively rich in organic matter, give high alcoxix indexes. Recently the writer determined the alcoxix indexes on a few samples of alkali soil, from areas which have been reclaimed and which are now highly productive, at the Citrus Experiment Station, Riverside, California. These gave indexes of about 300, about twice that of Brazilian alkali soils. High alcoxix index is an indication of good activity of the soil; and where such a condition exists, the reclamation of the soil should be feasible.

DISCUSSION

The alcoxix index is so designated because of the formation of Al-oxygen compounds similar to that represented by montmorillonite, $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, which is analogous to $2[(\text{SiO}_3)_2\text{Al}]\text{H}$, which in turn, can be compared with



divalent, or tetravalent, and may be combined with any base that happens to be present.

An alternate expression for the alcoxix index is *total activity* or *total activity* of the soil. We believe, however, that the method described does not give an exact measure of total activity or total acidity because some acid and some active compounds are soluble in alcohol and therefore can not be determined by this method.

By means of the alcoxix index we have sought a measure of the total activity of the soil. We believe that this index is superior to Hissink's *S* and *T* values and to $\text{Al} + \text{H}$ values, since each of these latter refer to only a part of the soil.

* Blanck, E. Handbuch der Bodenlehre, Bd. 3, S. 333.

With soil from Estado da Bahia, it was found that the different horizons must have been in equilibrium insofar as *S*, *T*, and *Al + H* values and alcoxix indexes are concerned, as shown by the following:

A horizon

Alcoxix index.....	350
<i>Al + H</i> value.....	26.5
<i>S</i> value.....	30.5

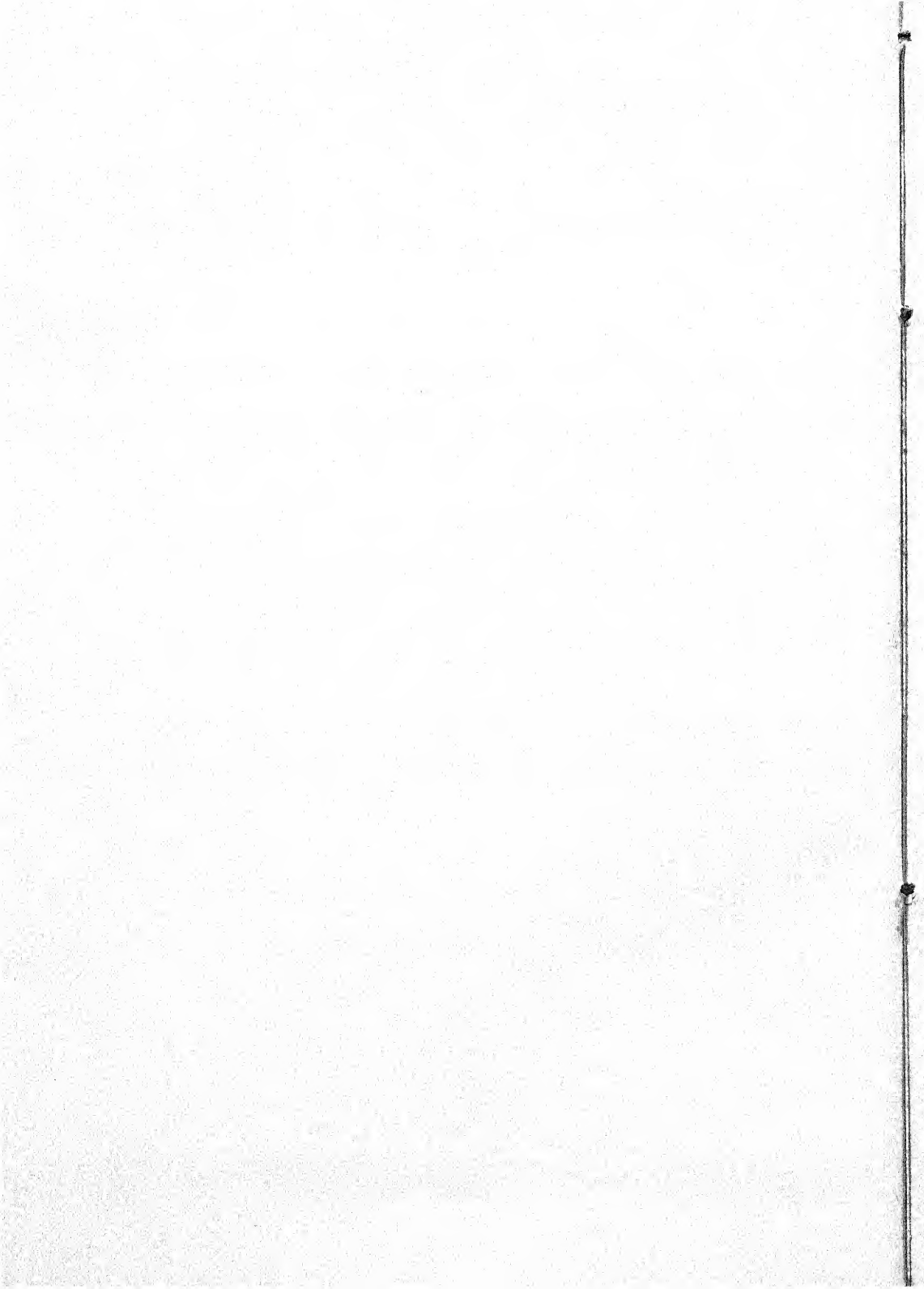
B horizon

Alcoxix index.....	850
<i>Al + H</i> value.....	67.0
<i>S</i> value.....	54.3

C horizon

Alcoxix index.....	650
<i>Al + H</i> value.....	46.5
<i>S</i> value.....	36.6

In several other tropical soils these values and the alcoxix index seemed, likewise, to be in equilibrium.



AN INDIRECT METHOD FOR DETERMINING THE MOISTURE CONTENT OF SOILS AT THE "STICKY POINT"

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The "sticky point" as a "single-value soil constant" has been studied by many British workers for its bearing upon tillage. A knowledge of such a physical property of the soil may be of direct help to farmers, as this constant seems to be an estimate of the maximum content of moisture for successful cultivation.

It is also known that the "sticky point" is highly correlated with many other physical properties of soils, such as loss on ignition, clay content, organic matter content, and the water content in equilibrium with an atmosphere of 50 per cent relative humidity (1). A measure of this constant, therefore, is indirectly a measure of the other properties and also gives a picture of the soil colloids.

The two methods in general use for determining the "sticky point" are that of Olmstead (3) and that of Keen and Coutts (2). The technic elaborated by Keen and Coutts is as follows: About 10 gm. of soil was spread in a thin layer on a glass plate, and distilled water was added from a fine jet until the soil was definitely wet and sticky. The mass was worked into a paste with a spatula and then scraped from the glass plate and kneaded by hand until the soil just reached the stage at which it no longer stuck to the hands or knife. The sample of kneaded soil was dried in an oven at 110°C. for 12 hours. It was weighed and the percentage of moisture calculated.

This procedure, though widely used at present, is not without defect, as seen from the following fact: In a statement made by Keen (1), when two samples of soil from the Rothamsted Station were sent to 14 stations in Europe and America for the determination of the "sticky point," the values obtained by different stations varied wide. The values of one sample ranged from 27 to 35 per cent, and those of the other had a still wider range. Because of this fact some precaution should be taken to prevent the personal error from causing such experimental difference.

It is the purpose of this paper to describe a method for locating the "sticky point," which is based upon the fact that when drops of water are slowly added to a plane surface of fine soil, a nearly hemispherical mass is formed which, if picked up and kneaded by hand, just reaches the stage at which it no longer sticks to the hands or the knife; that is, the soil is assumed to be at its "sticky point," as defined by Keen.

EXPERIMENTAL

Most of the samples used in this experiment were collected from the rice fields around Chu-yuan, in Kiangsu Province, and from Taipingmen, Nan-king, and some came from Shensi Province along the Wei River. The clay content of the samples, determined by the hydrometer method of Bouyoucos, was found to vary from 21.3 to 46.4 per cent. The organic matter content, determined by the hot potassium dichromate oxidation method of Allison, was found to vary from 0.5 to 4.0 per cent.

About 50 gm. of soil was passed through a 2-mm. sieve and placed in a small wire basket, 1-cm. mesh, resting in a shallow container. The surface of the soil was made smooth by scraping it with a plate. Then 1.0 cc. of distilled water was dropped from a burette, the tip of which was 1.5 inches above the soil surface, at a rate slow enough to allow the water to soak through. Experience showed that half a minute was quite enough. The mass was left intact for another half minute. The wire basket, gently tipped to let the dry soil filter through the bottom, was then lifted from the container, and the moistened soil was picked up with a pair of glass rods and weighed immediately.

Results obtained were greatly influenced by the rate at which the water dropped and by the compactness of the sample upon which the water was added. Precautions were taken, therefore, in every determination to ensure uniform rate and compactness. In cases where the results of the second determination were not so close to the first as desired, a third determination was made; the average of the three was generally satisfactory.

On the surface of the moistened mass formed, three concentric circles of different moisture content were observed (due to the unequal rate of diffusion of the water added); namely, the circle of supersaturation upon which the water dropped, the circle of saturation in the middle, and the outermost unsaturated circle. The circles were not transitional as expected, but were rather distinct even after the soil was dry. It was also found that the amount of superfluous moisture in the innermost circle just compensated for the unsaturation of the outermost circle after the whole mass was kneaded.

In the course of the determinations of the "sticky-point" constant in these samples, a number of difficulties were encountered. It was noted that the water, when dropped upon some of the samples (nos. 9, 11, 12, 17, and 25), did not diffuse so readily as in the other samples. Upon examination of the dried mass of these five samples, a white crust formation was noted on the surface, undoubtedly indicating the presence of soluble salts in the soils which hindered the ready diffusion of water. The soluble salts were removed by stirring 100 gm. of air-dried soil in 500 cc. of distilled water for 10 minutes and then filtering through a suction funnel. After that, the samples were air-dried, and determinations were again made as described above.

The moisture content of the air-dry soil should be determined beforehand. The moisture content at the "sticky point" is obtained by dividing the weight

TABLE 1

A comparison of the percentage moisture content at the "sticky point" by the indirect method and by the method used by Keen and Coutts

SOIL NUMBER	STICKY POINT BY THE INDIRECT METHOD		STICKY POINT BY KEEN AND COUTTS' METHOD		DIFFERENCE
		Average		Average	
1	34.5	34.7	34.0	34.4	-0.3
	35.0		34.8		
2	36.4	36.2	35.8	35.6	-0.6
	36.0		35.5		
3	32.1	31.7	32.0	32.5	+0.8
	31.3		32.9		
4	30.4	30.8	31.0	31.0	+0.2
	31.2		31.0		
5	32.5	33.0	32.4	32.2	-0.8
	33.5		32.0		
6	35.8	35.9	34.8	35.1	-0.8
	36.1		35.4		
7	30.1	31.0	30.4	30.6	-0.4
	32.0		30.8		
8	24.6	24.8	24.0	24.2	-0.6
	25.0		24.3		
9*	22.0	21.5	25.8	25.9	+4.4
	21.0		26.0		
10	32.0	31.0	32.4	32.2	+1.2
	30.0		32.0		
11*	33.1	33.5	36.4	36.6	+3.1
	34.0		36.8		
12*	30.1	31.0	35.9	36.4	+5.4
	32.0		36.9		
13	36.4	36.7	36.5	36.5	-0.2
	37.0		36.5		
14	27.4	27.8	26.0	26.4	-1.4
	28.5		26.8		
15	24.5	23.7	24.2	24.6	+0.9
	23.0		24.8		

* Samples contain large quantities of soluble salts.

TABLE 1—*Concluded*

SOIL NUMBER	STICKY POINT BY THE INDIRECT METHOD		STICKY POINT BY KEEN AND COUTTS' METHOD		DIFFERENCE
		Average		Average	
16	30.0	31.2	28.5	29.2	-2.2
	32.4		29.9		
17*	30.4	31.1	35.1	35.5	+4.4
	31.9		36.0		
18	24.3	24.8	23.9	24.0	-0.8
	25.4		24.0		
19	27.4	27.8	28.0	28.1	+0.3
	28.3		28.2		
20	26.4	25.7	25.0	24.6	-1.1
	25.0		24.2		
21	29.9	28.8	28.2	27.5	+1.3
	27.8		26.8		
22	36.9	37.0	36.4	36.2	-0.8
	37.2		36.0		
23	40.1	41.0	42.0	41.1	+0.1
	42.0		40.3		
24	46.7	46.8	45.0	45.1	-1.7
	47.0		45.2		
25*	30.4	29.7	33.2	33.6	+3.9
	29.0		34.0		
26	43.1	43.0	43.0	43.0	0.0
	43.0		43.0		
27	39.2	39.1	38.7	37.9	-1.2
	39.1		37.2		
28	45.2	44.1	45.2	44.6	+0.5
	43.0		44.0		
29	33.2	33.5	34.0	33.5	0.0
	34.8		33.0		
30	41.0	40.5	42.0	41.0	+0.5
	40.0		40.1		

of 1 cc. of distilled water at the specific temperature plus the weight of moisture originally contained in the air-dry sample, by the weight of soil on an oven-dry (110°C.) basis. For general purposes, assume that 1 cc. of distilled water equals 1.0 gm. The value calculated, times 100, gives the percentage of moisture content at the "sticky point" of the particular sample.

RESULTS AND DISCUSSION

From table 1 it is seen that the results obtained by the indirect method are in agreement with those obtained by the method used by Keen and Coutts, except for those samples already mentioned, which contained an excessive amount of soluble salts. Upon the removal of the soluble salts, the figures fell into agreement with those obtained by Keen and Coutts (table 2). This

TABLE 2
Percentage moisture content at the "sticky point" after removal of soluble salts

SOIL NUMBER	STICKY POINT BY THE INDIRECT METHOD		STICKY POINT BY KEEN AND COUTTS' METHOD		DIFFERENCE
		Average		Average	
9	25.4	25.2	25.6	25.8	+0.6
	25.0		26.0		
11	36.0	36.5	36.4	36.6	+0.1
	37.1		36.8		
12	34.2	35.1	35.9	36.4	+1.3
	36.0		36.9		
17	36.2	36.2	35.1	35.5	-0.7
	36.2		36.0		
25	33.0	33.3	33.2	33.6	+0.3
	33.7		34.0		

indirect method has other advantages: (a) The figures obtained by this method would represent nearly the field condition because of the fact that most of the natural granules remain intact, whereas in Keen and Coutts' determination the moistened soil is brought into a single-grain or muddled condition (4, p. 209), and the paste, consisting simply of soil and water, completely saturates the colloidal gel and fills the interstices—conditions which are rarely, if ever, attained under natural field conditions; (b) it is a rapid and economic method, as the constant is directly figured from the weight of the moistened soil mass.

The only defect of the indirect method is that it cannot be used for soils containing large quantities of soluble salts, since such soils require less water to become "sticky" than do soils with small quantities of soluble salts. The

amount of decrease in "sticky point" in proportion to increase in content of soluble salts is beyond the scope of the present study. The accuracy of this method is influenced by the rate at which the water drops and by the compactness of the soil.

SUMMARY

A rapid and economical method for determining the moisture content at the "sticky point" of soils is given. Results from this method are thought to represent nearly the state of moisture content under field conditions.

Results obtained by this indirect method were comparable with those obtained by the method used by Keen and Coutts.

The only defect of this method is that it cannot be used for soils containing large quantities of soluble salts.

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FOREST SOIL STUDIES: I. RELATION OF RATE OF DECOMPOSITION OF TREE LEAVES TO THEIR ACID-BASE BALANCE AND OTHER CHEMICAL PROPERTIES¹

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It is generally recognized that the most characteristic as well as the most important part of forest soils is the humus layer. The properties of this layer materially influence the amount of nutrients available for plant growth and, therefore, the growth and reproduction of the forest.

Although the factors affecting the development of different types of humus layers are not fully understood, it is generally believed that the tree cover plays an important role, possibly both directly and indirectly (11, 12, 13, 15, 17, 18, 23, 27). The mor type of forest humus is usually found under coniferous species and some deciduous trees, whereas the mull type is usually found under certain types of deciduous species. The reasons for these general relationships are not well established, although it is believed that the difference in the chemical composition of the leaf- and needle-fall of various species may be at least partly responsible for the differences in the humus layers formed. The properties that have been studied, mainly, are the calcium content and the acidity (1, 3, 4, 6, 7, 10, 26). These chemical properties are believed to affect the rate of decomposition of the litter and therefore the rate of liberation of nitrogen and other plant nutrients and the characteristics of the residual humus.

Romell (25), however, has recently criticized this concept of forest humus formation. According to his theory the differences in forest humus layers are not due to variations in the rate and amount of decomposition of the litter, but rather to the type of decomposition as determined by the action of different types of microorganisms. Romell contends that in mor the soil life is dominated by fungi which produce acidity, whereas in mull the fungus vegetation is relatively scarce, and bacteria play the dominant role. Very few data have been available in support of this theory. Even if it is assumed that the characteristics of the humus layer are determined by the character of the microbial population, this theory does not explain why different types of microorganisms predominate in litter from different tree species.

¹ Contribution from the department of agronomy and genetics, published with the approval of the director of the West Virginia Agricultural Experiment Station as Scientific Paper No. 217.

It is evident from these general remarks that a better understanding is needed of the various factors that determine the property of forest humus layers, and hence the productivity of forest soils. If the species of tree is an important controlling factor in determining forest-soil productivity, it is essential to obtain adequate information regarding the chemical composition of the litter of different species, their rates of decomposition, and the character of the decomposing residues.

Studies regarding the rate of decomposition of litter from different tree species have consisted mostly of field observations (6, 12, 17). Two investigations, however, have been reported of controlled studies in the laboratory. Lunt (19) studied the rate of decomposition of six hardwood species and found considerable difference among them. Melin (20), in a study of sixteen tree species, also found wide variations in decomposition, but found no correlation between such properties of the litter as pH, percentage of nitrogen, and total ash and the rate of decomposition.

Although some general relationships have been observed between the calcium content of the litter of various species and the type of humus layer developed, Plice (23), in a recent more comprehensive study containing an excellent literature review, found relatively poor agreement between the calcium content, or the calcium, magnesium, and potassium contents of the litter and the characteristics of the resulting humus.

The lack of a close relationship between such properties of the litter as its ash and calcium content, the rate of decomposition of the litter, and the nature of the residual humus is not entirely unexpected. Not only does the ash of various plants differ in content of silica, an element that has no effect on the acidity of the residue, but plants differ likewise in their content of different acidic and basic elements. Upon complete decomposition of plant materials the basicity of the residue would not be expected to be determined, therefore, by the total content of calcium but rather by the excess of the basic elements, primarily calcium, magnesium, potassium and sodium, over the acidic elements, chlorine, phosphorus and sulfur (all expressed on an equivalent weight basis).² Moreover, it has been shown by Waksman and coworkers (30, 31, 32), Norman (21), and others that the organic constituents of plants materially affect their rate of decomposition.

The objectives of this study are as follows: To determine the variation in the excess base, calcium, ash, H-ion concentration, nitrogen, and water-soluble organic matter of the litter of different tree species; to study the rate of decomposition of the fresh litter from different tree species under controlled conditions in the laboratory; and to determine the importance of the excess-base and other chemical properties of the litter in influencing the relative rates of decomposition of the litter from different forest-tree species.

² The excess of basic over acidic elements in plant materials will be referred to as "excess base" and will be expressed in milligram equivalents per 100 gm. of plant material.

GENERAL PROCEDURE AND METHODS

Samples studied

With two exceptions, the samples used in this study were collected from recently fallen leaves or from those that were mature and crisp but still attached to the tree. In collecting the leaves from the ground, care was taken to obtain only those that had recently fallen and had not been leached by rains. A brief description of the 31 samples used in this study is given in table 1. The majority of the samples were taken within a radius of 10 miles of Morgantown, West Virginia; the remaining samples, in other sections of the state. The soils from the Morgantown, Thomas, and Spencer areas are acid, unproductive silt and clay loams derived from shale and sandstone and classified in the Dekalb and Meigs series; those from Kearneysville and Hedgesville are more fertile clay loam soils derived from limestone and classified as Hagerstown silt loam. The acidity of the soils from the individual locations was not determined, but previous studies had shown that the pH of the soils in the former group ranges from about 4.8 to 5.4 and that of the soils in the latter group usually ranges from about 5.4 to 6.0.

The samples of leaves and needles were air dried and ground in a Wiley mill for the chemical and decomposition studies.

Chemical methods

The acid-base balance of the litter was determined by a method which is a slight modification of that developed by Frear (9). This consists essentially of igniting the sample for 60 minutes instead of the shorter period proposed by Frear. This assures more complete conversion of magnesium nitrate to magnesium oxide. Occasionally nitrate destruction is not complete; consequently a nitrate test is made after each ignition and if nitrates are found to be present in interfering amounts, a small quantity of carbon black is added, the solution is evaporated, and the residue is reignited.

The water-soluble organic matter was extracted by dialysis (22). One-gram samples of the leaves or needles were placed in collodion sacks inside 150-cc. extraction flasks. (The sacks had been made in 150-cc. extraction flasks.) Forty milliliters of water was put inside and 60 milliliters added outside the sack. The top of the collodion sack was folded against the side of the flask, and a stopper was inserted in such a manner that the flask could be shaken without any of the sample being lost. The flasks were shaken gently at 1-hour intervals for 6 hours and then allowed to stand for 18 hours. Fifty milliliters of the extract containing the soluble organic material was removed to a suitable weighed container (50-cc. beaker), evaporated to dryness, and weighed. The sample was then ignited and reweighed, and the difference between the two weights was taken as the weight of the water-soluble and dialyzable organic matter.

It can be seen from table 2 that the results obtained by the dialysis method

TABLE 1

Leaf samples studied for percentage decomposition and various chemical properties

LABORATORY NUMBER	SCIENTIFIC NAME	COMMON NAME	DATE SAMPLED	LOCATION	SOURCE*
1	<i>Acer rubrum</i> L.	Red maple	10-25-34	Morgantown	Ground
2	<i>Platanus occidentalis</i> L.	Sycamore	10-25-34	Morgantown	Ground
3	<i>Fagus grandifolia</i> Ehrh.	Beech	10-25-34	Morgantown	Ground
4	<i>Cornus florida</i> L.	Dogwood	10-25-34	Morgantown	Ground
6	<i>Quercus alba</i> L.	White oak	10-25-34	Morgantown	Tree
8	<i>Liriodendron tulipifera</i> L.	Yellow poplar	10-25-34	Morgantown	Ground
9	<i>Robinia Pseudo-Acacia</i> L.	Black locust	10-25-34	Morgantown	Tree
10	<i>Acer saccharum</i> March.	Sugar maple	10-25-34	Morgantown	Tree
11	<i>Quercus alba</i> L.	White oak	10-25-34	Morgantown	Tree
12	<i>Quercus borealis</i> Mishx.	Red oak	10-25-34	Morgantown	Tree
14	<i>Rhus hirta</i> Sudworth.	Staghorn sumac	10-25-34	Morgantown	Tree
15	<i>Fagus grandifolia</i> Ehrh.	Beech	10-25-34	Morgantown	Tree
16	<i>Sassafras variifolium</i> †	Sassafras	10-25-34	Morgantown	Tree
17	<i>Cornus florida</i> L.	Dogwood	10-25-34	Morgantown	Tree
18	<i>Acer saccharum</i> March.	Sugar maple	10-25-34	Morgantown	Ground
21	<i>Robinia Pseudo-Acacia</i> L.	Black locust	10-25-34	Morgantown	Tree
23	<i>Liriodendron tulipifera</i> L.	Yellow poplar	10-31-34	Morgantown	Ground
25	<i>Sassafras variifolium</i> †	Sassafras	10-31-34	Morgantown	Tree
26	<i>Quercus velutina</i> Lam.	Black oak	10-31-34	Morgantown	Tree
31	<i>Pinus virginiana</i> Mill.	Scrub pine	10-31-34	Kearneysville	Ground
32	<i>Pinus Strobus</i> L.	White pine	10-31-34	Hedgesville	Ground
35	<i>Platanus occidentalis</i> L.	Sycamore	10-19-35	Morgantown	Ground
36	<i>Aesculus Hippocastanum</i> L.	Horse chestnut	10-19-35	Morgantown	Tree
43	<i>Pinus rigida</i> Mill.	Pitch pine	10-11-35	Spencer	Tree
46	<i>Juglans nigra</i> L.	Black walnut	10-11-35	Spencer	Tree
47	<i>Juglans nigra</i> L.	Black walnut	10-11-35	Spencer	Tree
49	<i>Juglans nigra</i> L.	Black walnut	10-20-35	Spencer	Tree
51	<i>Juniperus virginiana</i> L.	Red cedar	11-12-35	Kearneysville	Tree
53	<i>Pinus virginiana</i> Mill.	Scrub pine	11-12-35	Kearneysville	Tree
55	<i>Quercus coccinea</i> Muench.	Scarlet oak	11-12-35	Kearneysville	Tree
58	<i>Pinus rigida</i> Mill.	Pitch pine	4- -36	Thomas	Tree

* All samples were well matured except nos. 9 and 21, which were slightly green.

† Salisb, Ktze.

TABLE 2

Content of water-soluble organic and inorganic material obtained by different extraction methods

SPECIES	ORGANIC MATERIAL		INORGANIC MATERIAL	
	Dialysis method	Waksman's method	Dialysis method	Waksman's method
	per cent	per cent	per cent	per cent
Beech.....	5.81	6.28	1.18	1.33
Red oak.....	7.59	9.96	0.58	1.09
Yellow poplar.....	20.68	19.56	7.31	8.29
Red maple.....	23.74	23.37	1.81	1.64

compare favorably with those obtained by the method developed by Waksman (29). With reasonably careful manipulation as to amount of shaking and period of dialyzing, good duplication can be obtained. This method eliminated the difficulty in filtering, which was encountered in Waksman's method, when working with samples of sassafras, oak, and maple leaves. The method is also well adapted to routine determinations.

Nitrogen was determined by the Kjeldahl method. For the determination of ash, 1-gm. samples were ignited for 5 hours at about 1000° F. Calcium was determined on the ignited ash by the regular procedure. Hydrogen-ion concentration was determined potentiometrically with the glass electrode using a 1 to 10 litter-water suspension.

Method of studying decomposition

Fifteen-gram samples of air-dry material were placed in suitable glass bottles, and the total weighed. Each was then inoculated with 1 cc. of the supernatant solution obtained by thoroughly shaking leaf mold with water and allowing the mixture to stand overnight. The leaf mold had been collected from underneath trees of most of the species studied. The sample in each bottle was then moistened to the extent of its water-holding capacity. The water-holding capacity was determined by placing 1-gm. samples into weighed Gooch crucibles containing a moist filter disk, soaking the samples in water for 24 hours, and drawing off the water by suction through the use of a water-pump. Several of the samples (Nos. 12, 16, 25, and 26) could not be satisfactorily freed from excess water, and the proper moisture content for each of these samples was therefore estimated. The amount of water used is given in the last column of table 5. After distilled water was added, the bottles were stoppered with cotton and incubated at 27–28° C. for the desired periods of time. The moisture content was maintained by adding water at irregular intervals. At the end of 2-, 4-, and 6-month periods the samples were removed from the bottles to large petri dishes to be air dried and the loss of weight determined.

EXPERIMENTAL DATA

Chemical properties of fresh litter

The chemical studies of the leaves selected for study are given in table 3. Most samples have pH values between 4.0 and 5.0, and a few pine samples have pH values below 4.0. The samples of highest pH values were yellow poplar, dogwood, horse chestnut, and black locust, one sample of the latter having a pH value of 6.68. These values are in surprisingly close agreement with those reported by Plice (23) for a number of these species.

The nitrogen content of the leaves varied from 0.46 per cent for a sample of pitch pine to 2.06 per cent for a sample of black locust. Other samples high in nitrogen are black walnut, staghorn sumac, and red cedar. Those conspicuously low are pitch pine, white pine, sugar maple, red maple, beech, and

white oak. Although there is considerable variation in some cases within a species, the differences between some of the species are very marked. Moreover, the values reported by Plice (23) for some of these species are very similar to the ones obtained in this study. Likewise, Coile (7) reported values for

TABLE 3
Chemical properties of the litter from different tree species

LABORATORY NUMBER	SPECIES	H-ION CONCENTRATION	N	WATER-SOLUBLE ORGANIC MATTER	ASH	Ca*	EXCESS BASE*
		pH	per cent	per cent	per cent	m.e.	m.e.
58	Pitch pine	3.46	0.57	7.7	1.94	23.4	38.2
43	Pitch pine	4.14	0.46	19.8	2.86	30.4	50.2
53	Scrub pine	3.75	1.08	11.7	2.74	19.1	40.4
31	Scrub pine	3.97	0.59	12.1	2.64	27.2	50.6
32	White pine	4.24	0.50	10.3	2.47	28.8	41.7
55	Scarlet oak	4.50	0.78	6.6	3.16	36.2	61.5
3	Beech	4.98	0.57	10.0	5.44	45.0	68.0
15	Beech	5.17	0.68	5.5	6.02	52.3	71.3
35	Sycamore	4.60	0.87	8.8	7.30	75.8	64.5
2	Sycamore	4.79	0.86	10.1	8.32	98.5	78.5
16	Sassafras	4.94	0.89	11.7	6.44	45.5	73.3
25	Sassafras	4.99	1.09	16.9	5.50	66.6	80.1
11	White oak	4.48	0.61	14.8	5.22	38.6	63.9
6	White oak	4.31	0.59	10.9	6.30	74.8	95.5
26	Black oak	4.79	0.83	13.4	3.68	41.4	88.3
51	Red cedar	4.89	1.24	9.0	5.15	73.4	99.0
12	Red oak	4.89	0.76	13.8	6.92	64.7	101.2
10	Sugar maple	4.24	0.45	20.2	8.72	84.6	107.3
18	Sugar maple	4.39	0.64	19.3	8.35	95.4	110.5
1	Red maple	4.70	0.57	26.4	8.09	86.7	113.3
8	Yellow poplar	5.19	0.74	26.2	5.32	75.4	109.6
23	Yellow poplar	5.30	0.85	23.9	6.34	97.7	131.5
14	Staghorn sumac	4.60	1.08	21.8	7.79	105.3	131.8
21	Black locust	5.24	2.06	19.8	6.04	117.4	137.5
9	Black locust	6.68	1.29	17.2	7.25	127.1	152.1
4	Dogwood	5.09	0.58	18.7	7.00	111.4	139.9
17	Dogwood	5.15	0.71	20.0	9.37	162.8	163.2
49	Black walnut	4.83	1.69	4.7	6.64	84.2	117.4
46	Black walnut	4.91	1.37	11.4	8.62	104.2	151.7
47	Black walnut	5.32	1.49	13.9	11.54	158.6	214.7
36	Horse chestnut	5.17	0.75	13.1	8.86	125.4	173.7

* Expressed as milligram equivalents per 100 gm. of the material.

red cedar, yellow poplar, and red maple which are in agreement with these figures. He obtained considerably higher values, however, for white oak and dogwood than were obtained in this study.

The percentage of water-soluble organic materials varies widely among species and also in some cases within species. Pitch pine No. 43 contained

19.8 per cent, whereas No. 58 contained only 7.7 per cent. The species with leaves particularly low in water-soluble organic materials are scarlet oak, beech, and sycamore; and those that are particularly high are sugar maple, red maple, yellow poplar, sumac, dogwood, and black locust.

The ash content of the litter of various species varied from 1.94 per cent for one of the pitch pine samples to 11.54 per cent for a sample of black walnut. The pine samples are all low in ash. Of the hardwood samples, scarlet oak (3.16 per cent) and black oak (3.68 per cent) are the lowest. Red and sugar maple, sycamore, dogwood, and black walnut contained the highest amounts. These results are in general agreement with those of other workers (2, 17, 19, 21). Joffe (17) found in his studies that the average ash content of conifers was 2.54 per cent, with a range of 1.29 to 3.31 per cent, whereas the average for hardwoods was 6.63 per cent, with a range of 3.85 to 11.74 per cent.

The calcium content of the various samples is expressed as milligram equivalents per 100 gm. of material in order to enable ready comparison of the values with those of excess base. The pine samples have a calcium content of about 25 m.e. Some of the hardwoods also are low in calcium, particularly scarlet oak, black oak, beech, sassafras, and white, red, and black oak. Intermediate in content of calcium are sycamore, red cedar, sugar maple, red maple, and yellow poplar. The species relatively high in calcium are staghorn sumac, dogwood, black walnut, black locust, and horse chestnut. A comparison of these values with those reported in the literature for certain of these species shows that the calcium content varies considerably within a species, a result apparently of site differences and other factors (1, 10, 15, 23). In spite of such variations, however, species differences are evident. For example, pines, oaks, and beech are relatively low in calcium, whereas such species as sugar maple, yellow poplar, and dogwood are generally high.

The values for excess base are given in the last column of table 3. It will be noted that the range is from 38.2 m.e. per 100 grams for a sample of pitch pine to 214.7 for a sample of black walnut. The significance of this difference can readily be understood when it is considered that upon complete decomposition the black walnut sample would liberate over five and one-half times as much base for neutralizing soil acidity as would the pitch-pine sample.

There is a general relationship between the total ash, the calcium, and the excess-base content of the different samples of litter. A statistical analysis of the data shows that the correlation is highly significant. When individual samples are considered, however, marked discrepancies are apparent. For example, samples 26, 31, and 53 contain about half as much calcium as excess base, whereas samples 2 and 35 contain more calcium than excess base. Likewise, samples 15, 16, and 35 contain approximately the same amount of ash as samples 23, 14, and 21, although the latter contain nearly twice as much excess base as the former. These variations are what may be expected, for it is well known that plants vary considerably in the relative amount of different bases and also in their contents of the acidic elements, chlorine, sulfur,

and phosphorus. Moreover, the ash content of plants varies considerably because of differences in their content of silicon, an element that has no effect on the excess-base value.

For ease of discussion the 19 species were arranged in three groups according to their excess-base values as shown in table 4.

TABLE 4
Grouping of trees with respect to the excess-base content of the leaves

GROUPS	NUMBER OF SAMPLES	SPECIES	EXCESS BASE	DECOMPOSITION AFTER 6 MONTHS
				<i>per cent</i>
<i>Group 1</i>	1	White pine	42	17
Less than 75 m.e. excess base per 100 gm. material	2	Pitch pine	44	21
	2	Scrub pine	46	25
	1	Scarlet oak	62	27
	2	Beech	70	17
	2	Sycamore	72	21
		Average	56	21
<i>Group 2</i>	2	Sassafras	77	45
75-110 m.e. excess base per 100 gm. of material	2	White oak	80	28
	1	Black oak	88	29
	1	Red cedar	99	40
	1	Red oak	101	36
	2	Sugar maple	109	33
		Average	92	35
<i>Group 3</i>	1	Red maple	113	45
More than 110 m.e. excess base per 100 gm. of material	2	Yellow poplar	121	55
	1	Staghorn sumac	132	60
	2	Black locust	145	47
	2	Dogwood	152	43
	3	Black walnut	161	47
	1	Horse chestnut	174	30
		Average	143	47

Decomposition studies

The percentage decomposition of the tree leaves after 2, 4, and 6 months is reported in table 5, in which the species are arranged in the same order as in tables 3 and 4. It will be noted that the most rapid decomposition with all samples occurred during the first 2 months. This is well shown in figure 1. Many of the samples, mostly those showing a high decomposition, underwent about two-thirds as much decomposition during the first 2 months as during the whole 6-month period. A very marked difference in decomposition exists among the different species. After the 6-month period the fresh litter from

beech, sycamore, and the pines had undergone less than 25 per cent decomposition. In contrast, the litter from yellow poplar and staghorn sumac had undergone over 50 per cent decomposition. In the range of 25 to 40 per cent

TABLE 5
Amounts of decomposition and changes in pH value of litter from different tree species after various periods of time

GROUP	LABORATORY NUMBER	SPECIES	pH VALUE OF ORIGINAL LEAF MATERIAL	pH VALUE AFTER VARIOUS PERIODS OF DECOMPOSITION		DECOMPOSITION AFTER VARIOUS PERIODS			H ₂ O CONTENT DURING DECOMPOSITION
				4 mo.	6 mo.	2 mo. per cent	4 mo. per cent	6 mo. per cent	
1	58	Pitch pine	3.46	4.86	5.04	5.3	12.9	17.1	150
	43	Pitch pine	4.14	5.96	5.90	15.9	21.4	25.2	110
	53	Scrub pine	3.75	5.32	5.18	14.9	21.5	24.6	150
	31	Scrub pine	3.97	5.56	5.42	12.6	20.0	24.9	150
	32	White pine	4.24	5.56	5.32	6.0	13.0	17.2	160
	55	Scarlet oak	4.50	4.79	4.99	12.0	20.7	26.5	300
	3	Beech	4.98	6.17	6.16	7.0	12.3	17.1	250
	15	Beech	5.17	6.77	6.65	7.3	13.3	17.0	250
	35	Sycamore	4.60	5.72	5.68	7.6	14.3	17.8	220
	2	Sycamore	4.79	6.22	6.02	12.0	19.0	23.2	220
2	16	Sassafras	4.94	7.24	7.00	28.6	39.1	45.9	270
	25	Sassafras	4.99	7.26	6.85	27.6	38.0	43.4	270
	11	White oak	4.48	5.03	5.11	13.8	22.2	27.0	280
	6	White oak	4.31	5.28	5.61	12.6	22.4	28.3	280
	26	Black oak	4.79	6.40	6.25	16.0	23.3	29.1	300
	51	Red cedar	4.89	7.83	7.64	25.8	34.8	40.4	150
	12	Red oak	4.89	7.44	7.20	22.2	30.4	36.4	300
	10	Sugar maple	4.24	4.65	5.48	15.5	25.7	31.8	290
	18	Sugar maple	4.39	5.82	5.92	18.2	29.1	34.7	290
3	1	Red maple	4.70	6.72	6.98	27.5	39.5	44.9	240
	8	Yellow poplar	5.19	8.50	8.08	38.5	50.8	55.9	290
	23	Yellow poplar	5.30	8.28	8.05	36.4	48.7	53.9	290
	14	Staghorn sumac	4.60	8.54	8.77	46.6	55.8	59.5	160
	21	Black locust	5.24	8.12	8.16	34.3	43.6	49.6	200
	9	Black locust	6.68	7.52	7.60	30.6	38.2	44.4	200
	4	Dogwood	5.09	5.94	6.72	25.6	36.1	43.8	240
	17	Dogwood	5.15	4.21	5.52	25.3	34.7	41.3	240
	49	Black walnut	4.83	7.96	7.79	30.5	42.6	49.7	170
	46	Black walnut	4.91	7.15	7.33	22.8	32.8	41.6	170
	47	Black walnut	5.32	9.05	8.92	27.1	41.5	48.3	170
	36	Horse chestnut	5.17	8.57	8.64	10.4	21.1	29.8	300

decomposition are found sugar maple, horse chestnut, and the oaks; in the range of 40 to 50 per cent decomposition are sassafras, red maple, dogwood, black walnut, and black locust.

It is interesting to compare some of these values with those obtained by Lunt (19) and by Melin (20) for certain of the species. Working with leaves from six hardwood species, Lunt found during a 7-week decomposition period that the greatest loss of dry matter occurred with red maple and dogwood, and the least with beech and white oak. Sugar maple was intermediate. Melin found that red maple leaves decomposed very fast; sugar maple was intermediate; and beech, pitch pine, and white pine were slow, except one sample of white pine containing a high percentage of nitrogen. The agreement between the results obtained by these investigators and those obtained in this

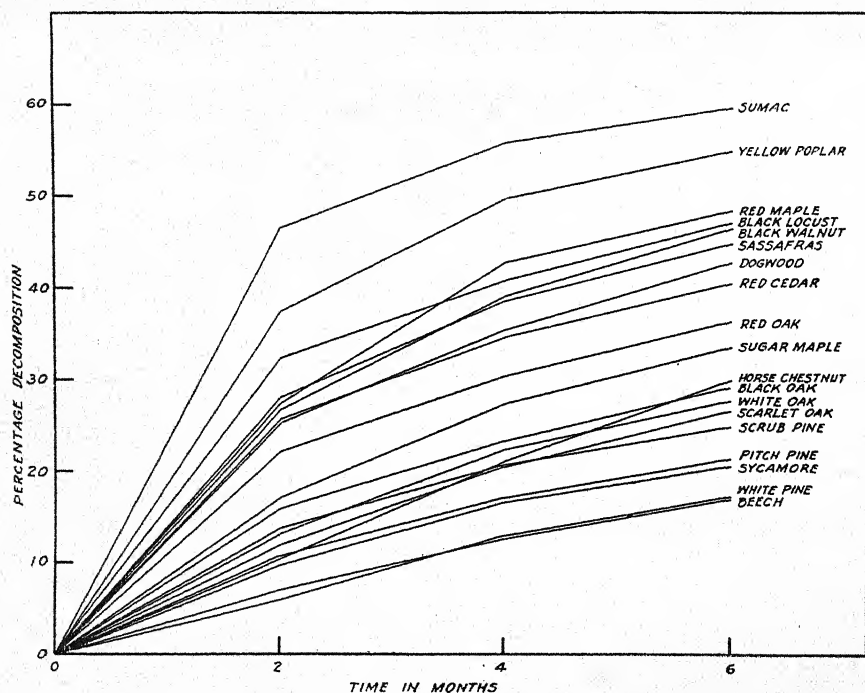


FIG. 1. AVERAGE RATE OF DECOMPOSITION OF LITTER FROM DIFFERENT TREE SPECIES

study is very significant, particularly when it is considered that the conditions were quite different in the various investigations.

The pH values of the original leaf material and of the decomposing residues after 4 and 6 months' decomposition are also given in table 5. It will be noted that the acidity of the litter decreased markedly during the first 4-month period. In many cases the increase in pH is from two to over three units. The pH values after 6 months are not very different from those after 4 months, and in a number of cases are actually lower. This can readily be explained by the relatively small amount of decomposition between 4 and 6 months and by the fact that the salt concentration was probably higher after the 6-month

period than after the 4-month period. The effect of salt concentration on the pH of certain of the samples is shown in table 6. Though differences of the order noted here would not be obtained by the increase in salt content between the 4- and 6-month periods, the principle probably applies.

It is well to note that, in general, the samples having the highest pH values after decomposition are also the ones having the highest amounts of excess base. Thus, most of the samples of group 1 with relatively low amounts of excess base had pH values below 6.0 after 6 months' decomposition, whereas those in group 3 had pH values generally above 7.5. The coefficient of correlation between the H-ion concentration of the residual humus material

TABLE 6
Effect of leaching on the pH values of leaf litter (after 4 months' decomposition)

LABORATORY NUMBER	SPECIES	pH VALUES	
		Before leaching	After leaching
58	Pitch pine	4.86	5.19
43	Pitch pine	5.96	6.27
53	Scrub pine	5.32	5.69
31	Scrub pine	5.56	5.94
32	White pine	5.56	5.90
55	Scarlet oak	4.79	5.52
3	Beech	6.16	6.79
15	Beech	6.77	6.97
11	White oak	5.03	5.58
6	White oak	5.28	5.78
35	Sycamore	5.72	6.27
2	Sycamore	6.22	6.51
16	Sassafras	7.24	7.46
25	Sassafras	7.26	7.63
26	Black oak	6.40	6.74
12	Red oak	7.44	7.64
10	Sugar maple	4.65	5.20
18	Sugar maple	5.82	6.34
14	Staghorn sumac	8.54	8.54

and the excess base of the fresh litter was found to be -0.55 , a highly significant value. A very high correlation would, of course, not be expected at this stage of decomposition, since the different residues were found to have quite different base-exchange capacities.³

Relationship between rate of decomposition and chemical composition of litter

The relationship between the rate of decomposition of the litter of different species and their content of excess base is shown roughly in table 4. The group of low excess-base content shows an average decomposition of 21 per

³ Unpublished data.

cent during 6 months; the intermediate group, 35 per cent; and the group of high excess-base values, 47 per cent. This relationship is seen in figure 2.

In order to determine more definitely the relationship between percentage decomposition and the excess base and other properties of the litter, the simple

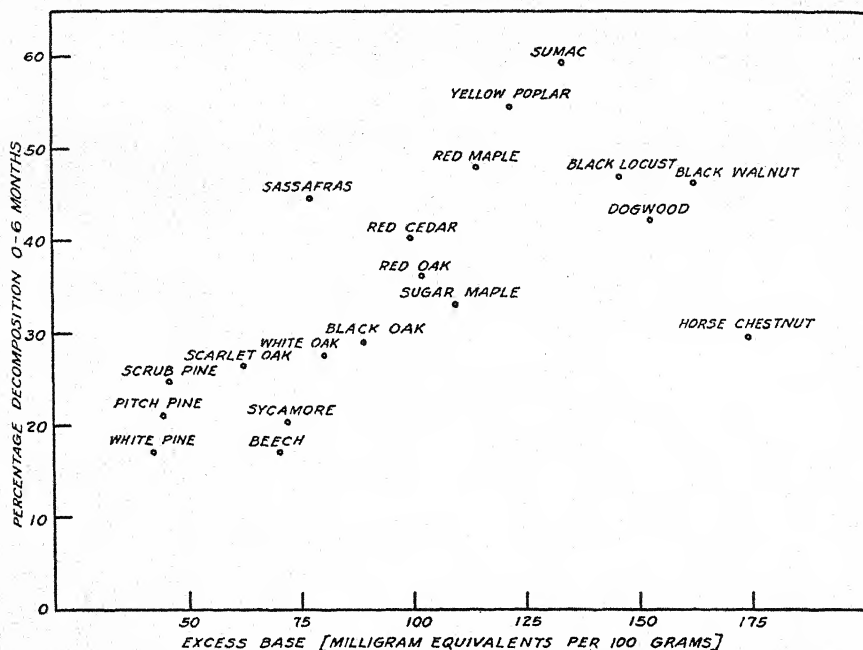


FIG. 2. RELATION BETWEEN PERCENTAGE DECOMPOSITION AND EXCESS BASE OF LITTER FROM DIFFERENT TREE SPECIES (AVERAGE VALUES)

TABLE 7

Simple coefficients of correlation between decomposition and chemical properties of tree litter

RELATIONSHIP	SYMBOL FOR RELATIONSHIP	0-6-MONTH PERIOD OF DECOMPOSITION
Percentage decomposition and excess base	r_{xa}	0.672
Percentage decomposition and water-soluble organic matter	r_{xb}	0.599
Percentage decomposition and total nitrogen	r_{xc}	0.527
Percentage decomposition and total ash	r_{xd}	0.460
Percentage decomposition and total calcium	r_{xe}	0.589

The least value that can be considered *significant* is 0.355; and the least that can be considered *highly significant* is 0.456.

coefficients of correlation were first determined. These are shown in table 7. It will be noted that there is a highly significant correlation between decomposition and each of the five independent variables. The highest correlation is between excess base and percentage decomposition, the coefficient of correlation being 0.672, and the lowest is between total ash and decomposition.

A further analysis of the data by periods and also a study of the combined effect of two and of three of the independent variables on decomposition are given in table 8. During the 0-2-month period there is a highly significant correlation between decomposition, on one hand, and excess base, water-soluble organic matter, and total nitrogen on the other. During the 2-6-month period, the coefficient of correlation between decomposition and the excess-base content was 0.767, which is considerably greater than that during the

TABLE 8

Coefficients of simple and multiple correlation between decomposition and various chemical properties of tree litter

RELATIONSHIP	SYMBOL FOR RELATIONSHIP	COEFFICIENT OF CORRELATION		MINIMUM VALUES NECESSARY FOR SIGNIFICANCE*	
		0-2- month period	2-6- month period	S	H S
I. Simple correlations:					
Per cent decomposition and excess base.	r_{za}	0.564	.767	0.355	0.456
Per cent decomposition and water-soluble organic matter.....	r_{zb}	0.619	.307	0.355	0.456
Per cent decomposition and per cent nitrogen.....	r_{zc}	0.522	.334	0.355	0.456
II. Multiple correlations:					
Per cent decomposition and excess base + water-soluble organic matter.....	$r_{z.ab}$	0.712	.767	0.439	0.530
Per cent decomposition and excess base + nitrogen.....	$r_{z.ac}$	0.772	.768	0.439	0.530
Per cent decomposition and water-soluble organic matter + N.....	$r_{z.bc}$	0.853	.478	0.439	0.530
Per cent decomposition and excess base + water-soluble organic matter + N.	$r_{z.abc}$	0.854	.768	0.498	0.582
III. Other relationships:					
Excess base and water-soluble organic material.....	r_{ab}	= 0.387			
Excess base and nitrogen.....	r_{ac}	= 0.457			
Water-soluble organic material and nitrogen.....	r_{bc}	= 0.101			

* The values under S are the least that can be considered significant; the values under H S are the least that can be considered highly significant.

first 2 months; whereas the coefficient of correlation with water-soluble organic material dropped from 0.619 to 0.307, and the coefficient of correlation between decomposition and percentage nitrogen dropped from 0.522 to 0.334, or below the limits of significance. It is apparent, therefore, that the influence of the nitrogen and of the water-soluble organic matter content of the litter on decomposition is exerted largely during the first 2 months, and that thereafter the decomposition is much more closely associated with the excess-base content of the litter.

The coefficients of multiple correlation between percentage decomposition and the three independent variables show that for the first 2 months there is a much better correlation between any two independent variables and percentage decomposition than between any one of them and decomposition. This is particularly so when the nitrogen and the water-soluble organic matter are considered together. If only the last 4 months are considered, however, the simple correlation between percentage decomposition and excess base is just as high as the multiple correlations ($r_{x.ab}$, $r_{x.ac}$, and $r_{x.abc}$) which take into consideration percentage nitrogen and water-soluble organic matter in addition to excess base. The coefficient of multiple correlation $r_{x.bc}$ for the 2-6 month period is found to be relatively low, 0.478, and much lower than the simple correlation between decomposition and excess base, 0.767. This again emphasizes the importance of the excess base and decomposition relationship during this 2-6-month period.

TABLE 9

Relative effects of independent variables on decomposition expressed as percentage*

VARIABLE	SYMBOL	0-2-MONTH PERIOD	2-6-MONTH PERIOD	0-6-MONTH PERIOD
Excess base.....per cent	A	4	97	19
H ₂ O-soluble organic matter.....per cent	B	51	1	44
Nitrogen.....per cent	C	45	2	37
Total.....		100	100	100

* Calculated from Standard partial regression coefficients.

The coefficient of multiple correlation between the three independent variables and percentage decomposition is 0.854 for the first period and 0.768 for the 2-6-month period.

The relative effects of the independent variables on percentage decomposition were calculated by use of the standard regression coefficients (28). The relative values expressed as percentages are given in table 9. For the entire 6-month period the relative percentage values are for excess base 19, water-soluble organic material 44, and nitrogen 37. It should be emphasized, however, that even though the relative effect of excess base is less than that of water-soluble organic matter and nitrogen, the coefficient of simple correlation for excess base and decomposition is greater, being 0.672 as compared to 0.599 and 0.527 for the other two variables. This apparent contradiction can be explained by the fact that excess base is significantly correlated with water-soluble organic matter and total nitrogen content, whereas nitrogen and water-soluble organic matter are not related.

The data of particular interest are those for the individual periods. During the 0-2-month period the water-soluble organic material and total nitrogen accounted for virtually all the explained variations in decomposition. During

the 2-6-month period, however, excess base is the determining factor, making up 97 per cent of the combined effects of all three. Percentage nitrogen and water-soluble organic matter have decreased to insignificance in this period.

These relationships can probably be explained by the chemical changes that take place as decomposition progresses and by the consequent change in flora. During the early period of decomposition the water-soluble organic constituents are readily attacked. Because of the high acidity, fungi are probably dominant and very active in this decomposition, and since they build up a large amount of fungal tissue a relatively large amount of available nitrogen is needed. Lack

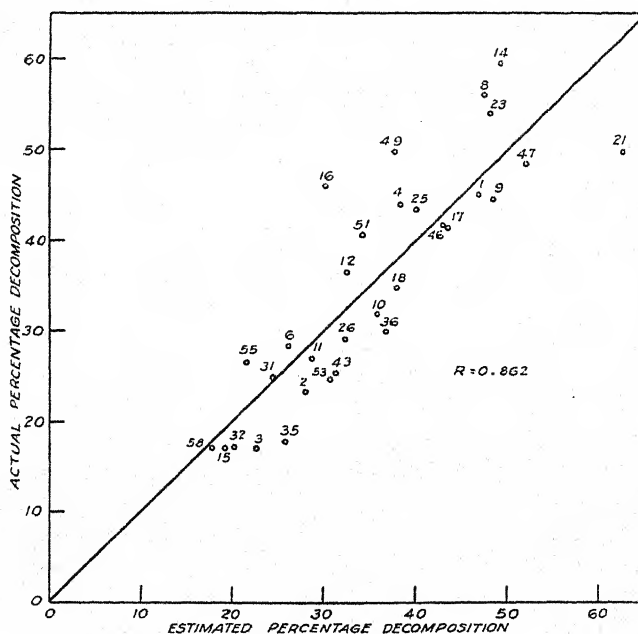


FIG. 3. PERCENTAGE DECOMPOSITION ESTIMATED FROM EXCESS BASE, PERCENTAGE OF WATER-SOLUBLE ORGANIC MATTER, AND PERCENTAGE OF NITROGEN AS INDEPENDENT VARIABLES

of nitrogen, therefore, is readily reflected in decreased rate of decomposition, which explains the correlation between nitrogen and decomposition during the first 2-month period. The lack of such correlation in the 2-6-month period is probably explained by the fact that the rate of decomposition has decreased and that bacteria rather than fungi now constitute the active microbial flora because of the lower acidity and also by the fact that there are smaller amounts of easily decomposable organic constituents. Nitrogen therefore is less of a limiting factor, and the acidity of the media, which, as is well known, influences bacterial activity, becomes more important. Since, as previously shown, the acidity of the decomposing residue is related to the excess-base content of the

original litter, a good correlation between excess base and decomposition would be expected.

From the multiple regression equation ($X = .0705A + 1.1894B + 15.680C - 2.9572$) it is possible to calculate the percentage decomposition of the various tree litters. These calculated values are plotted against the actual values in figure 3. For the 0-6-month period the multiple correlation between percentage decomposition and the three independent variables is 0.862.

GENERAL DISCUSSION

It is evident from the data obtained in this investigation that the fresh litters of different forest-tree species vary considerably in rate of decomposition. These differences are particularly significant when compared with the observed effect of these tree species on the character of the soil humus layer. The mor type of humus layer is found not only under pines and most other coniferous trees but also under many hardwood stands of oaks and beech (6, 8, 14, 16, 18, 23, 32). The latter species have been found in this investigation to produce litter which decomposes somewhat faster than pine litter but much more slowly than litter of many other hardwoods.

Griffith, Hartwell, and Shaw (12) classified a number of plots predominating in different forest-tree species into three groups, on the basis of the depth of the dark brown soil zone. The species in group A, none of which is represented in the present study, produced a deeper dark brown soil zone than those in the other groups. It is particularly significant that group B, which included soft and hard maple, generally produced deeper dark brown zones than trees in the C group of plots, which contained a preponderance of red oak, white oak, beech, white pine, and chestnut.

The high rate of decomposition of yellow poplar, black locust, dogwood, and black walnut obtained in this investigation is also in agreement with the observed effect of these species in producing a mull type of humus layer. Thus Coile (7) found that in the Duke Forest a mull type of humus layer is formed under dogwood, and a mor-like humus layer under pine and oak. Many field observations have also shown that the litter of black locust and black walnut rapidly decomposes, the residue becoming readily incorporated into the mineral soil. During the progress of a pasture survey in West Virginia it was observed that bluegrass was usually much better under these trees than in the open pasture. In the case of black locust this might be explained partly by the increased nitrogen content of the soil (13). With both species, however, the high excess-base content and the rapid rate of decomposition of the litter undoubtedly resulted in the liberation of bases and other plant nutrients favorable to the growth of Kentucky bluegrass, a species that requires a less acid and better soil than the other species present in these pastures.

The data obtained in this investigation tend to disprove Romell's theory regarding the formation of various types of forest humus layers. Romell (24, 25) contends that the rate of decomposition of the litter is not greater in the

formation of mull than in mor and that the difference in the characteristics of mull and mor is due, therefore, to the type of decomposition rather than to the rate and amount of decomposition. He believes that the type of decomposition is determined by the kind of microorganisms active in decomposition, and refers to his concept as a biological one contrasted to what he describes as the present "chemical or physico-chemical" concept. It is obvious, of course, that the so-called chemical concept, which recognizes the influence of the chemical properties of the litter in affecting rate of decomposition, does not minimize the importance of different types of microorganisms in bringing about these changes. It does emphasize, however, that variation in type of microorganisms or in their activity is a result of environmental conditions and that one of the important environmental factors is the chemical property of the litter.

One of the arguments proposed by Romell in support of his theory is that it explains more adequately than other theories the beneficial effects on the humus layer of such forestry measures as burning and green-slash manuring. Green-slash manuring is believed by him to induce a change in the type of decomposition by weakening or killing the fungi belonging to the mor vegetation. He postulates that the beneficial effect cannot be due to a higher base content, since the lime content of green needles and leaves is lower than that of mature litter. As shown in this study, however, the lime content is not the only chemical property of the litter affecting rate of decomposition. In some additional studies to be reported from this station it has been found that green leaves and needles decomposed considerably faster than mature litter, a difference at least partly explained by differences in water-soluble organic matter and other organic constituents. Green slash may therefore promote the decomposition process in the underlying litter by liberating bases and other constituents as it decomposes, which would be favorable to the activities of the microorganisms present. Similarly the beneficial effects obtained by light burning can be attributed at least partly to the liberation of bases which favorably affect rate of decomposition.

Although these data emphasize the importance of tree species in influencing the formation of forest humus layers, it should be recognized that the effect of different tree species is not independent of site. Wide variations in site conditions may affect the rate of decomposition of the litter directly through variations in moisture, temperature, and other environmental factors. Moreover, the site may indirectly influence the decomposition by influencing the chemical composition of the litter.

The good correlation obtained between certain chemical properties of the litter and the rate of decomposition is of particular interest. It emphasizes the value of chemical studies of tree litter in determining the relative effect of different species on the soil. Though field work is essential in obtaining a better understanding of soil-tree relationships, there is no question that controlled studies in the laboratory and green house can be of very much value.

This is especially evident when it is considered that under field conditions such a mixture of species exists that it is often difficult to determine the effect of individual species. Coordinated chemical, bacteriological, and physical studies, both in field and laboratory, are essential if a better understanding is to be obtained of soil-tree relationships.

SUMMARY

Thirty-one representative samples of mature undecomposed leaves and needles, representing 19 species, were studied, first in regard to differences in certain chemical properties, and second in regard to their rates of decomposition under controlled conditions. The chemical properties studied were H-ion concentration, total nitrogen, water-soluble organic matter, ash, calcium, and excess base. The decomposition as measured by loss of original material was determined after periods of 2, 4, and 6 months. Studies were made of the relationship between the chemical properties of the litter and the rate of decomposition.

The pH value of the different samples varied from 3.46 to 6.68, with most of the values below 5.0. The nitrogen content varied between 0.45 per cent for a sample of sugar maple to 2.06 per cent for a sample of black locust; the ash content, from 1.94 per cent for a sample of pitch pine to 11.54 per cent for a sample of black walnut; the calcium, from 19.1 m.e. per 100 gm. for a sample of scrub pine to 162.8 m.e. for dogwood; and the water-soluble organic matter, from 4.7 per cent for a sample of black walnut to 26.4 per cent for a sample of red maple. The excess-base content of the different samples varied from 38.2 m.e. per 100 gm. for a sample of pitch pine to 214.7 m.e. for a sample of black walnut. The values for excess base are of particular interest, since they represent the amount of base available for neutralizing soil acidity upon complete decomposition of the litter.

Although some variation exists in the chemical composition of different samples from the same species, more marked differences were found between different species and genera with respect to total nitrogen, ash, calcium, and excess base. The variations in water-soluble organic matter between different samples of the same species are considerable and may be greater than those between different species. This is probably to be expected, since a slight variation in the maturity of the sample when collected would affect the content of water-soluble organic constituents.

The pH of the residual material, in general, increased progressively as decomposition proceeded. There was no definite relationship between the pH of the original material and the pH of the residual organic matter, but a significant relationship between the latter and the excess-base content of the original litter. Those leaves high in excess base generally gave, upon decomposition, a residue of high pH value; and those low in excess base, a low pH value.

A marked difference was obtained in the rate of decomposition of fresh leaf litter from various forest-tree species when maintained under controlled condi-

tions and inoculated uniformly with a forest humus suspension. After the 6-month period, for example, the decomposition averaged less than 25 per cent for samples of pitch pine, scrub pine, white pine, beech, and sycamore; whereas it averaged over 45 per cent for samples of yellow poplar, staghorn sumac, black locust, and black walnut. Moreover, it was found that this variation in rate of decomposition is explained largely by variation in the chemical properties of the litter.

Of the properties of the litter studied, those most closely associated with rate of decomposition are water-soluble organic matter, percentage of nitrogen, and excess-base content. During the first 2 months of decomposition the first two were the controlling factors, the multiple coefficient of correlation being 0.85; whereas during the 2-6-month period the dominant factor influencing rate of decomposition was the excess-base content of the litter, the simple coefficient of correlation being 0.77.

The multiple coefficient of correlation between percentage decomposition during the 6-month period and the three independent variables—nitrogen, water-soluble organic matter, and excess base—was found to be 0.862.

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- (33) WATT, A. S. 1934 The vegetation of the Chiltern Hills, with special reference to the beechwoods and their seral relationships. *Jour. Ecology* 22: 445-507.

BOOKS

Principles of Organic Chemistry. By H. P. STARCK, Head of the Science Department, The Technical College, Kingston on Thames; formerly Lecturer in Chemistry, The Technical College, Bradford. Chemical Publishing Co., N. Y., 1938. Pp. viii + 664. Price \$5.

This volume is a combination of a textbook and a laboratory manual in organic chemistry. Such an arrangement has a distinct advantage. The exhaustive questions at the end of each chapter are another desirable feature in a text which is designed for students taking an introductory course in organic chemistry. The author is to be congratulated on the manner of introducing the subject. He is ready to face the criticism of being too elementary. One might feel that a student beginning the study of organic chemistry should be familiar with such elementary concepts as molecular formulas and weights. The truth of the matter is that students, as a rule, fail to review their earlier courses, and a repetition is frequently a desirable feature, especially if it is, like that of the author, concise and clear. The book is well illustrated. It contains a special chapter on general tests for organic substances, a series of tables, a description of the Svedberg ultracentrifuge, and an important appendix on first aid in the laboratory.

J. S. JOFFE

The Oxidation States of the Elements and Their Potentials in Aqueous Solutions.

By WENDEL M. LATIMER, Professor of Chemistry, University of California. New Prentice-Hall, Inc., 1938, Pp xiv + 352. Price \$3.

The primary object of this volume, as stated by the distinguished author whose name figures prominently in calculations of free energy and entropy, "is to gather the large mass of free-energy data which is scattered throughout the literature and to present it in a simple form as an aid in the interpretation of inorganic chemistry." One should not, however, be under the impression that this volume is merely a handbook of figures. Far from it. The volume is a treatise on the subject, and all the elements are discussed in the twenty-one chapters. Any worker engaged in studies of oxidation-reduction potentials will find this book of great help.

J. S. J.

Organic Chemistry. By PAUL KARRER, Professor in the University of Zurich. Translated from the latest German edition by A. J. Mee, Head of the Science Department, Glasgow Academy. "Elsevier"—Amsterdam, Nordemann Publishing Co., Inc., New York, 1938. Pp. xx + 902. Price \$11. A unique feature of this volume is the modesty of the translator. There is

not a word from him. Apparently he felt it would be superfluous for him to justify the translation of a book on organic chemistry which since 1928, the date of the first edition, has gone through six editions.

The aim of the book as seen by the distinguished author is stated in the preface to the English translation: "To provide students with a textbook of organic chemistry of medium size which would give them a survey of the ever increasing body of facts." One might question the terminology "medium size" as applied to a volume of 902 pages. Indeed, the author covers extensively the numerous phases of organic chemistry. The subject matter is presented in a very clear and readable style.

The book is divided into four parts: Part I: Aliphatic Compounds; Part II: Carbocyclic Compounds; Part III: Heterocyclic Compounds; Part IV: Organic Compounds with Heavy Hydrogen. Part IV, naturally brief because of the newness of the subject, occupies five pages. A series of tables cover such subjects as compounds definitely present in coal-tar, arranged in order of boiling points; world production of coal, 1936; sugar production; relative sweetness of various organic substances; poisonous substances used in warfare; important dates in the history of organic chemistry. These are only a few of the many tables given. Throughout the book, special stress is laid on the description of methods of preparing the compounds and on the chemistry of the naturally occurring substances. The biological aspect of organic chemistry is thus merged with biochemistry.

There are, of course, some errors in a volume of this kind. On page 1 the author speaks of acetic acid fermentation and of the "souring of wine by the agency of acetic fungus." The microbiologist might point out that in acetic acid fermentation the bacteria are the agents, not the fungi. This error simply means that an organic chemist need not necessarily be a microbiologist.

The book is a worthwhile addition to our stock of translations of scientific contributions from foreign languages.

J. S. J.

The Chemical Formulary. A collection of valuable, timely, practical commercial formulas and recipes for making thousands of products in many fields of industry. Volume IV. H. BENNETT, Editor-in-chief. Chemical Publishing Co., New York, 1939. Pp. 638. Price \$6.

The purpose of this publication is indicated by the subtitle. The book contains a wealth of recipes collected from various sources, of which the editor appropriately says: "Since these sources are often subject to various errors and omissions, due regard must be given to this factor." Many odd things one would not even think of may be found in this volume. In the section "Farm and Garden," the reviewer found such an oddity in the following formula for a soil conditioner: "coal ground to pass a screen of approximately 40 to 70 mesh and roasted at a temperature between 300 and 400 degrees F." What

this formula and another containing "rock salt" will do to the soil is not stated. The volume even has formulas for the latest fad on hydroponics or "soilless growing nutrient salts." A soil scientist would not advise use of the "Farm formulas" without reservations and without consultation with an expert. The editor justly foresees such circumstances and advises the reader to "arrange for the services of a chemist or technical worker familiar with the specific field in which he is interested."

J. S. J.

Annual Review of Biochemistry. Volume VIII. JAMES MURRAY LUCK, Editor, Stanford University, and JAMES H. C. SMITH, Associate Editor, Carnegie Institution of Washington, Division of Plant Biology, Stanford University, California. Annual Reviews, Inc. Stanford University P. O., California, 1939. Pp. ix + 676. Price \$5.

The wide scope of these now famous "Annual Reviews" may be judged from the table of contents, which follows: Biological Oxidations and Reductions; Proteolytic Enzymes; Nonproteolytic Enzymes; Polysaccharides and Lignin; X-Ray Studies of the Structure of Compounds of Biological Interest; The Chemistry of the Acyclic Constituents of Natural Fats and Oils; The Chemistry of Proteins and Amino Acids; The Chemistry and Metabolism of the Compounds of Sulfur; Carbohydrate Metabolism; Lipid Metabolism; Metabolism of Proteins and Amino Acids; Mineral Metabolism. Calcium, Magnesium, and Phosphorus; Hormones; Choline as a Dietary Factor; The Water-Soluble Vitamins; Fat-Soluble Vitamins; Metabolism of Brain and Nerve; The Alkaloids; Chemical Aspects of Photosynthesis; Mineral Nutrition of Plants; Growth Hormones in the Higher Plants; Animal Poisons; Ruminant Nutrition; Immunochemistry; The Biochemistry of Yeast.

This volume is a worthy successor to the volumes of other years. The cosmopolitan nature of the Reviews is evident from the fact that eleven of the twenty-five papers are from foreign countries. To the specialists in the various fields of biochemistry these reviews are an invaluable aid.

J. S. J.

Utilization of Fats. By H. K. DEAN. With a foreword by T. P. Hilditch, Campbell-Brown Professor of Industrial Chemistry at the University, Liverpool. Chemical Publishing Co., New York, 1938. Pp. xiv + 292. Price \$6.

In a field of study which is in the process of expansion and development, as is the study of fats, a new volume is a welcome addition. The new theoretical aspects of the subject, especially the physicochemical reactions, have been incorporated in this volume. This makes the publication more valuable both from the theoretical and the applied side of the subject. The industrial applications of fatty materials and their derivatives form the main body of information in the following chapters: I. Constituents and Properties of Fats;

II. Analytical Methods; III. Classification, Composition, and Analysis of Fats; IV. Artificial Fats; V. Extraction and Refining of Fats; VI. Edible Fats; VII. Paint and Varnish Oils; VIII. Soaps and Fatty Acids; IX. Miscellaneous Applications.

By the use of small-sized type, the publishers, who are the exclusive agents for this book in North and South America, economized on the number of pages but not on the subject matter.

J. S. J.

Grundriss der tropischen und subtropischen Bodenkunde (An outline of Tropical and Subtropical Soils). Zweite, vermehrte Auflage. By P. VAGELER. Verlagsgesellschaft für Ackerbau m.b.h., Berlin, 1938. Pp. 252. Preis des Leinenbande RM 12.75.

The second, somewhat enlarged, edition of this scholarly monograph includes data on the tropical soils of Asia, Africa, and South America. A noteworthy feature of Dr. Vageler's work is that the author speaks authoritatively from personal experience. In the first edition he wrote about his studies in the tropics of Asia and Africa. In this edition he has added his observations on South America. He is associated now with the Agricultural Tropical Research Institute in Brazil, Instituto Agronomico de Estado de Sao Paulo in Campinas. The first edition was translated into English, and it is hoped that the second edition will not have to wait long. Anyone interested in tropical soils will profit by the presentation of Dr. Vageler.

J. S. J.

Report on Agricultural Research in Great Britain. A survey of its scope, administrative structure and finance, and of the methods of making its results known to farmers, with proposals for future development. By the Research Group of P E P (Political & Economic Planning). P E P, 16 Queen Anne's Gate, London, S.W.1, 1938. Pp. 154. Price 8s. 6d. net.

The title of this publication is a good summary of its content. The "Political and Economic Planning" group is a nonpartisan assembly of industrialists, distributors, officers of the central and local government, scientists, university teachers, and other professionals interested in the advancement of the various phases of social and economic activities. Their findings are presented in reports; and in the case of agriculture, they have attempted, as stated by the secretary, "to show how the links between agricultural research on the one hand and agricultural policy and practice on the other might be strengthened."

The report is, in a way, incomplete, inasmuch as the reader feels that not all that the investigators wanted to say was said. And yet it is a useful service rendered, and administrators of agricultural research may find enough food for thought in all that is in the report. It may not be amiss to end this brief review with an excerpt from a paragraph on page 104: "that the gap between the farmer on the one side and the research worker and the administrator on

the other is still too wide, is clear from the cumulative evidence of the facts assembled in this report. The fundamental questions, how to bring research to closer grips with the problems of the land, and how to make farmers sufficiently alive to the benefits of research to support it spontaneously, still await a satisfactory solution."

J. S. J.

Land Utilization in China. Volume 1. By JOHN LOSSING BUCK, Professor of Agricultural Economics, The University of Nanking. The University of Nanking, Nanking, China, 1937. Agents in the United States, The University of Chicago Press, Chicago. Pp. xxxii + 494, tables 207, maps 21, figs. 57, photos 62. Price \$5.

This volume, the first of a series of three, presents a study of land utilization in China as exemplified by 16,783 farms in 168 localities and 38,256 farm families in twenty-two provinces in China, 1929-1933. The survey method, used in this study, was amplified by such other data as were available for the purpose. Thus the subject of soils was treated by James Thorp, whose book *Geography of the Soils of China* represents an independent investigation outside of this survey.

The report of the study is presented in 15 chapters under the following headings: Chinese Agriculture; Agricultural Regions; Topography; Climate; Soils; The Land; Crops; Livestock and Fertility Maintenance; Size of Farm Business; Farm Labor; Prices and Taxation; Marketing; Population; Nutrition; The Standard of Living. Most of the material, 8 of the 15 chapters, was written up by Buck. The volume is beautifully illustrated.

It is a comprehensive study commensurate with its broad sponsorship by the University of Nanking, the Institute of Pacific Relations, National Economic Council, Central Bank of China, Milbank Memorial Fund, and others.

Besides the facts collected, the survey makes specific recommendations. One wonders how an invaded China could carry out the sound and well-wishing advice of this survey.

J. S. J.

Soil Science Society of America Proceedings 1938. Volume 3. Papers presented at meeting held in Washington, D. C., November 16-18, 1938. The Soil Science Society of America, G. G. Pohlman, Sec.-Treas., Morgantown, W. Va., 1939. Pp. x + 368. Price \$5.

Why a volume of this kind should open with a paper on "The Application of Agronomy in Farm Planning" is perhaps not the question for a reviewer to ponder. The explanation of the anomaly perhaps lies in the announcement on page 359 that the veteran editor of the *Journal of the American Society of Agronomy*, J. D. Lockett, was elected editor of the Proceedings.

It is questionable whether papers read by title should be included in the respective sections. A list at the end of the volume would serve the purpose

of recording these. One other question may be raised: Why is the abstract (in the table of contents this is not indicated) of the Appleman and Sear paper entitled "Microbiological Aspects of the Morrow Plot Soils" placed in the section on soil chemistry?

Aside from the minor adverse criticisms suggested, this volume is well arranged and the topics are well balanced. Whatever fault one may find with the contributions, he should remember that the presentation of a paper is almost tantamount to publication, and the editorial committee is handicapped.

Like the earlier proceedings, this volume is lithoprinted, of 8.5 x 11" size, well done, and with a sturdy and beautiful binding.

J. S. J.

Organicheskoe Veshchestvo Pochv (Organic Matter of Soils). By I. V. TYURIN. Sel'khozgiz, Leningrad, Moscow, 1937. Pp. 287. Price (unbound) 4 rubles 75 Kop. (about \$1).

From the subtitle, we find that this Russian publication deals with "the role of organic matter in soil formation and soil fertility." The subtitle is indeed fitting.

This volume is unique inasmuch as it comes from the pen of Prof. Tyurin, an outstanding pedologist, forestry student, and trained chemist. Heretofore, treatises on humus were written by chemists, bacteriologists, or the old type soils man, each of whom threw some light on the subject from his particular angle. And yet, humus is primarily associated with soil-forming processes and soil fertility. Of course, Prof. Tyurin is aware of the microbiological processes as the agencies of humus formation. He devotes chapter II, about 60 pages, to the "processes responsible for the conversion of organic residues in the soil." In the remainder of the chapters (chapter I is devoted to the "composition of organic residues entering the soil") Prof. Tyurin analyzes critically the following subjects: III. Chemical composition of humus; IV. Methods of analyzing and investigating humus; V. The role of humus in the soil-forming processes; VI. The role of humus in the fertility of the soil.

A commendable feature of the presentation is its straightforwardness. The subject is not "loaded"; it is full of meat well presented with an analytical discussion of the contributions.

The author writes from first-hand experience, in close contact with the soil, with the broad outlook of the Russian school of soils and an interest which extends to the deepest roots of the science.

In congratulating the author on his achievement, the reviewer regrets that this excellent concise treatise on humus is not available in the English language.

J. S. J.

Behold Our Land. By RUSSELL LORD. With an introduction by William Allen White. Houghton Mifflin Company, Boston, 1938. Pp. 310, illus. Price \$3.

A seasoned writer of popular articles on agriculture, the author of this very

readable story of our land has fulfilled the plan and purpose of the book, which in the early pages he outlines as follows:

I have undertaken to write a ground-line narrative of conquest and losses on the body of our land. It tells how long the weather takes to make a yielding soil; how rapidly nearly any soil, manhandled, may be lost to human use; and what, with great stretches of American soil washing or blowing out from under us, we have hastily developed as measures of defensive husbandry.

The story starts with stardust and ends in the troubled present. I do not offer it as a complete account. It skips, and seeks to avoid the merely technical. It is not a history, or an almanac or a work of science. It is more nearly . . . a "profile"—an action and character sketch—which takes as its subject a living piece of land, its formation, occupation, and changing growths.

The profile form permits individual interpretations which are not always susceptible to proof. But I do suggest, here and later, that other forms of erosion accompany the occupation and despoliation of a soil, and that, as a land becomes older, more crowded, more worn and wounded, accelerated erosion may extend beyond the physical surface of the country and attack the free spirit.

The book contains many excellent illustrations and a list of recommended reading.

H. B. KITCHEN

German-English Science Dictionary. By LOUIS DE VRIES, Professor of Modern Languages, Iowa State College. McGraw-Hill Book Company, Inc., New York and London, 1939. Pp. x + 473. Price \$3.

This dictionary for students in the agricultural, biological, and physical sciences, containing 48,000 entries, was compiled with the collaboration of members of the graduate faculty of Iowa State College. The author points out in his introduction that the work, the first dictionary of its kind, makes no claim to completeness but includes all basic information needed in finding meanings of compound words, which "because of their compactness and conciseness, are especially adapted to the requirements of scientific literature and enlarge scientific vocabularies constantly." A convenient-sized volume, it is printed in clear readable type, which should contribute much to its usability.

H. B. K.

Statistical Technique in Agricultural Research. By D. D. PATERSON, Reader in Agriculture at the Imperial College of Tropical Agriculture, Trinidad, B.W.I. McGraw-Hill Book Company, New York and London, 1939. Pp. x + 264. Price \$3.

One of the McGraw-Hill Publications in the Agricultural Sciences, this book is an elementary exposition of statistical technique for the average research worker who is interested in the practical application of the subject rather than in mathematical theory. The topics treated include the general principles of statistics, analysis of variance, goodness of fit and contingency tables, diagrams, correlation, regression, field experiments, serial and perennial crop experiments,

and recent developments in field experimentation. A bibliography, an appendix of statistical tables, and an index are also included. The book with its numerous examples of typical statistical problems encountered should be of considerable value to the research worker in designing and interpreting his experiments.

H. B. K.

Growing Plants Without Soil. The A.B.C. of Plant Chemiculture (Soilless Agriculture, Chemiculture, Water Culture, Hydroponics, Tank Farming, Sand Culture) Including Plant Growth Hormones and Their Use. By D. R. MATLIN. Chemical Publishing Company, New York, 1939. Pp. 140. Price \$2.

The growing of plants in solution and sand cultures, long used by scientists for the experimental study of plant nutrition and recently developed for the growing of plants for more practical purposes, has captured the public fancy. This volume for the layman, like many other popular presentations of the subject, views the advantages of the method through rose-colored spectacles.

H. B. K.

The World Was My Garden. Travels of a Plant Explorer. By DAVID FAIRCHILD. With a foreword by Elizabeth and Alfred Kay. Charles Scribner's Sons, New York, 1938. Pp. xiv + 494, illus. Price \$3.75.

In this fascinating autobiography, the author, who for more than 20 years was in charge of the Division of Plant Exploration and Introduction, of the United States Department of Agriculture, tells of his travels throughout the world in search of plants suitable for growth in America. More than 200 photographs, most of them taken by the author, illustrate this very human story of an agricultural explorer.

H. B. K.

Bacterial Metabolism. Second Edition. By MARJORY STEPHENSON, Associate of Newnham College, Cambridge, Member of the Scientific Staff of the Medical Research Council. Longmans, Green and Company, London and New York, 1939. Pp. xii + 392, illus. Price \$7.50.

Substantial advances in the field of bacterial biochemistry, especially in the study of bacterial growth, bacterial fermentations, bacterial enzymes, and nitrogen fixation, and the discovery of bacterial photosynthesis necessitated the entire rewriting of *Bacterial Metabolism*, which was first published in the "Monographs on Biochemistry" series in 1930. This second edition now appears as an advanced textbook.

Applied Mycology and Bacteriology. By L. D. GALLOWAY, Imperial Mycologist, New Delhi, 1934-1937, Mycologist to British Cotton Industry Research Association, 1927-1934, and R. BURGESS, Dairy Bacteriologist to

Lancs. County Council, Microbiologist to British Woollen Industry Research Association, 1927-1935. Distributed by Chemical Publishing Company, New York (exclusive agents in North and South America for this book), 1938. Pp. x + 186. Price \$4.

An elementary review of the essentials of mycology and bacteriology with particular reference to the scope and methods of economic microbiology.

Animal Life in Fresh Water. A guide to fresh-water invertebrates. By HELEN MELLANBY, Department of Zoology, University of Sheffield. With a foreword by L. E. S. Eastham, Professor of Zoology, University of Sheffield. Chemical Publishing Company, New York (exclusive agents in North and South America for this book), 1938. Pp. vii + 296, figs. 211. Price \$3.50.

A guide to the identification of the common fresh-water invertebrates with notes on their habits and distribution, written in elementary terms especially for school pupils.

An Introduction to Industrial Mycology. By GEORGE SMITH, Research Demonstrator, Department of Biochemistry, London School of Hygiene and Tropical Medicine. With a foreword by Harold Raistrick, University Professor of Biochemistry, London School of Hygiene and Tropical Medicine. Edward Arnold & Co., London, 1938. Pp. xii + 302, figs. 127. Price 16s net.

A textbook, for those beginning the study of "molds" rather than of fungi in general, consisting principally of descriptions and illustrations of genera of molds occurring in industrial products.

A Fundamental Approach to Bacteriology. By COURTLAND SAWIN MUDGE, Dairy Bacteriologist in the Experiment Station and Associate Professor of Dairy Industry, University of California, and FLOYD RUSSELL SMITH, Junior Dairy Bacteriologist in the Experiment Station and Instructor in Dairy Industry, University of California. J. W. Stacey, Inc., San Francisco, 1939. Pp. ix + 266, figs. 17.

A laboratory guide for instructors and students in general bacteriology.

The Biology of Bacteria. An Introduction to General Microbiology. Second Edition. By ARTHUR T. HENRICI, Professor of Bacteriology, University of Minnesota. D. C. Heath and Company, New York. Pp. xiii + 494, figs. 112. Price \$3.60.

In the revision of this textbook, two new chapters on ecology of bacteria have been added.

Research and Statistical Methodology Books and Reviews 1933-1938. Edited by OSCAR KRISSEN BUROS. Rutgers University Press, New Brunswick, 1938. Pp. viii + 100. Price \$1.25.

A collection of excerpts from critical reviews of research and statistical

methodology books and monographs published between January 1, 1933 and November 15, 1938.

Plant Physiology. By BERNARD S. MEYER, Associate Professor of Botany, the Ohio State University, and DONALD B. ANDERSON, Professor of Botany, College of Agriculture and Engineering of the University of North Carolina. D. Van Nostrand Company, New York, 1939. Pp. x + 696, figs. 151. Price \$4.50.

A textbook for colleges and universities, designed to serve as the basis for a conventional recitation course or as a background source of information for student reading in connection with lecture-discussion courses.

Introduction to Floral Mechanism. By S. G. JONES. Chemical Publishing Co., Inc., New York, 1939. Pp. xi + 274, illus. Price \$4.

This elementary textbook on floral morphology, by a member of the Department of Botany at the University of Glasgow, gives due consideration to the increasing emphasis on cytology and genetics in botany. The book is well supplied with illustrations, principally from original drawings by the author.

The Structure of Economic Plants. By HERMAN E. HAYWARD, Professor of Botany, The University of Chicago. The Macmillan Company, New York, 1938. Pp. x + 674, figs. 340. Price \$4.90.

The main part of this work, following the introductory chapters on general plant anatomy, deals with the structure and developmental anatomy of the economic plants, corn, wheat, onion, hemp, beet, radish, alfalfa, pea, flax, cotton, celery, sweet potato, white potato, tomato, squash, and lettuce, each selected on the basis of economic importance, suitability as a representative of the family to which it belongs, and intricacy of its anatomical and morphological detail. Important fruit crops have been omitted because of the author's plans to include them in a second volume.

Die Bierhefe als Heil-, Nähr- und Futtermittel (Brewer's Yeast as Medicine, Food, and Fodder). Second, Revised and Enlarged, Edition. By JULIUS SCHÜLEIN. Theodor Steinkopff, Dresden and Leipzig, 1938. Pp. viii + 262, figs. 22, tables 10. Price RM 9.

Bergey's Manual of Determinative Bacteriology. A Key for the Identification of Organisms of the Class Schizomycetes. By DAVID H. BERGEY, ROBERT S. BREED, and E. J. D. MURRAY. Williams & Wilkins Co., Baltimore, Md. Pp. ix + 78. Price \$1.

This is a reprint from the fifth edition of the Manual.

Plant Growth-Substances. Their chemistry and applications, with special reference to synthetics. By HUGH NICOL, Assistant Bacteriologist, Roth-

amsted Experimental Station. Distributed by Chemical Publishing Company, New York, 1938. Pp. xii + 106, illus. Price \$2.

Technical, for the most part, but containing two chapters for the layman.

Muir's Bacteriological Atlas. Second Edition. Atlas enlarged and text rewritten by C. E. VAN ROOYEN, M. D., Halley Stewart Research Fellow and Lecturer in Bacteriology, University of Edinburgh. William Wood & Company, Baltimore, Maryland, 1937. Pp. xvi + 90, pl. 83. Price \$5.25.

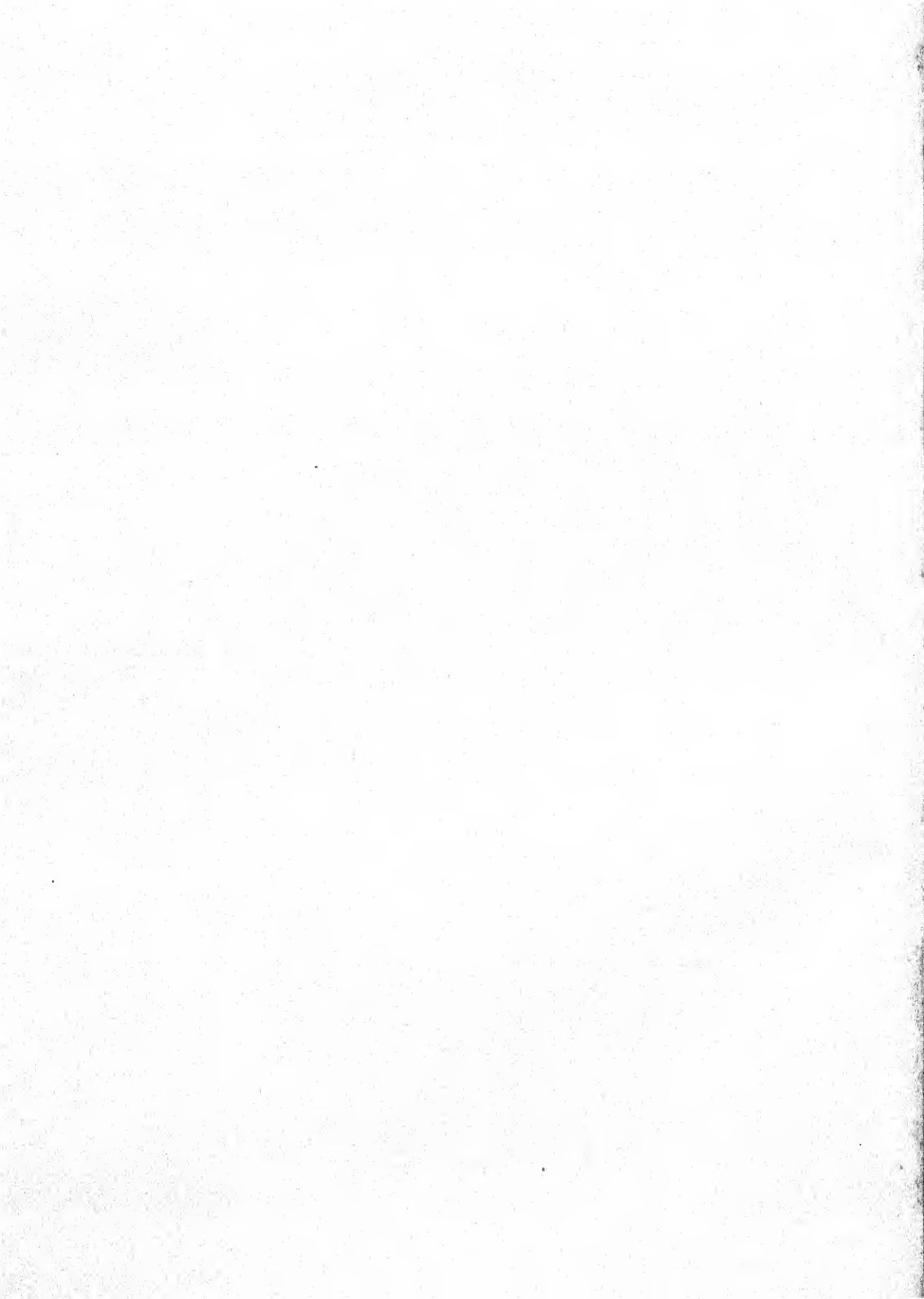
In the second edition of this atlas for medical undergraduates and others engaged in the study of practical bacteriology, the text has been rewritten, and twenty-six new colored plates illustrating the morphology of thirty-two different microorganisms have been added. Plates illustrating the elementary and inclusion bodies of various virus infections are a feature of this edition.

Modern Sewage Disposal. Edited by LANGDON PEARSE. Federation of Sewage Works Associations, 654 Madison Avenue, New York, N. Y. Pp. 372, illus.

This anniversary volume, issued to commemorate ten years of service by the Federation of Sewage Works Associations, is, according to the forward, "an effort to replace a convention of world-wide workers by a contributed set of papers along unusual topical lines." The papers are grouped under the following main headings: Sewage Treatment Practice, Sewage Research, Regional and National Aspects, and Industrial Wastes.

Cattle Fodder and Human Nutrition. With Special Reference to Biological Nitrogen Fixation. By ARTTURI I. VIRTANEN, Professor at the Technical University, Director of the Biochemical Institute, Helsinki. Cambridge University Press, Cambridge, 1938. Pp. 108, illus. Price \$2.25.

This book contains four lectures on the following subjects: The Mechanism of the Biological N-Fixation; The Symbiosis of the Leguminous Plants with the Legume Bacteria; The Production of Vitamins in Agriculture, with Special Reference to Human Nutrition; and The A.I.V. Method for the Preservation of Fresh Fodder and its Importance in Agriculture. A general survey is added in which the connection between the subject matter of the different lectures is illustrated and the practical importance in agriculture and human nutrition is discussed.



SOIL GENESIS FROM ANDESITE IN GRENADA, BRITISH WEST INDIES

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The island of Grenada in the British West Indies offers excellent material for the study of soil genesis from basic igneous rocks under a humid tropical climate having alternate wet and dry seasons. The commonest rocks comprise Pleistocene andesitic and basaltic lava-flows, the profound weathering of which has given rise to thick masses of red earth, from which fertile soils, mainly planted in cacao, have evolved. A typical example of a red earth profile has been examined by the writers in continuation of investigations begun in British Guiana (7).

DESCRIPTION OF THE PROFILE

The site of the profile is a new road cutting through a descending spur near the 12th milepost on the St. Georges-Grenville Road in St. David's Parish, Grenada, at an elevation of 750 feet, where the annual rainfall is about 70 inches.

(i) The *parent rock* is a porphyritic augite-andesite, in which augite occurs as large, black, lozenge-shaped phenocrysts (15.5 per cent), set in a fine-grained, gray, feldspathic matrix consisting of labradorite (73 per cent), with accessory magnetite (7.5 per cent) and yellow olivine (4 per cent). The rock shows columnar and spheroidal jointing, and its upper parts have disintegrated into rounded boulders, the average diameter of which is 2 feet and which have split into concentric shells.

(ii) The outermost of these shells are covered with friable crusts of *primary laterite*, 1 to 3 cm. thick, colored golden-yellow, and studded with bright red-brown powdery patches, presumably comprising hydrous iron oxide residues derived from the augite phenocrysts.

(iii) Passing outward from the laterite-encrusted boulders, is a heterogeneous coherent mass, 1 to 4 feet thick, of *pink earth*, consisting of finely speckled groundmass colored pale red, blue-gray, and gray-white, in which altered augite crystals are still conspicuous as rust-brown spots. Certain areas of this

¹ The authors wish to acknowledge their indebtedness to G. Milne, of the East African Agricultural Research Station, Amani, Tanganyika, for collecting the materials of the red earth profile during a visit to Grenada in April, 1938, and for many helpful discussions; also to C. E. Marshall, of the Missouri State Agricultural College, Columbia, for the gift of mineral specimens and for valuable advice.

zone show brighter intermerging patches, colored russet, red-brown, orange, and yellow, presenting a kaleidoscopic aspect.

(iv) Upward, the pink earth passes into a layer, 2 to 8 feet thick, of homogeneous brick-red to pale reddish brown clay loam (*red earth*) showing a rough columnar structure with a brittle, coarsely granular substructure.

(v) The red earth grades into a uniform dark red-brown loamy surface soil, 1 to 5 feet thick, showing a well-developed crumb, consisting of stable angular fragments. The soil is covered with a thin leaf litter, and supports dense secondary bush.

Representative samples of the different parts of the profile were procured in the middle of the dry season of 1938 for laboratory examination and labelled (i) parent rock, (ii) laterite, (iii) pink earth, (iv) red earth, and (v) soil.

EXPERIMENTAL PROCEDURES

The samples were examined by chemical, physical, and mineralogical methods, and by the application of dye tests, including the alizarin test elaborated by us in 1931 (5). The chief aim was the complete identification of the specific mineral components, both primary and secondary, of each of the five kinds of material.

Subsamples were ground to pass a 100-mesh sieve, and colloidal clay fractions, upper size limit $2\ \mu$, were separated by dispersion in sodium carbonate solution with mechanical agitation, followed by appropriate settling in beakers. The clay suspensions were evaporated, treated with acetic acid, filtered, washed, oven-dried, and weighed. The sand and the silt fractions were also dried and weighed. For mineralogical analysis, subsamples were merely crushed, dispersed, and fractionated by a sieve and beaker method into three sand grades (minimum size $10\ \mu$), a silt grade, and a fine silt and clay grade (maximum size $5\ \mu$). The sand grades were cleaned with boiling hydrochloric acid for examination under the microscope.

Chemical analysis

Both the whole materials and the colloidal clay fractions were quantitatively analyzed after sodium carbonate fusion by standard methods of silicate analysis. Quartz was determined by the tri-acid method (7). Magnetite was removed from the whole material prior to fusion and was determined separately. Gibbsite alumina was estimated, after ignition, by the alizarin method. The analytical data obtained are presented in table 1, and losses and gains are expressed in table 2, on the assumption that total alumina remains constant during the transformations. Table 3 expresses the results in terms of component minerals, assuming kaolinite to be the chief secondary mineral generated.

Mineralogical analysis

The magnetite content of the five grades of each of the materials was determined by abstracting the mineral first with a small bar magnet, and then with

TABLE 1
Bulk chemical composition of red earth profile samples

SAMPLE	PERCENTAGE COMPOSITION										MOLECULAR RATIOS*						
	SiO ₂		Al ₂ O ₃		Fe ₂ O ₃		TiO ₂	CaO	MgO	K ₂ O + Na ₂ O	H ₂ O		SiO ₂ / Al ₂ O ₃	Fe ₂ O ₃ / Al ₂ O ₃	SiO ₂ / H ₂ O	Al ₂ O ₃ / H ₂ O	
	Quartz	Com- bined	Gibbsi- tic	Com- bined	Magnet- ite†	Other					Gibbsi- tic	Other					
<i>Whole material</i>																	
(i) Parent rock.....	...	44.1	16.9	7.5	1.8	1.2	14.5	7.7	4.8	1.4	4.42	0.07	9.42	2.1	2.1
(ii) Laterite.....	2.8	15.5	24.9	11.3	13.0	10.4	2.5	(1.4)	(1.4)	...	13.2	4.8†	2.32	0.59	0.97	0.42	0.42
(iii) Pink earth.....	1.1	33.5	3.0	29.3	9.3	8.6	1.1	(0.7)	(0.7)	...	1.6	11.4†	1.94	0.19	0.88	0.45	0.45
(iv) Red earth.....	2.8	30.0	3.3	27.1	8.7	10.6	1.3	0.3	2.2	...	1.7	11.0†	1.89	0.25	0.82	0.43	0.43
(v) Surface soil.....	3.3	29.0	2.0	22.3	6.9	15.4	(1.9)	0.4	2.5	...	1.1	11.1†	2.20	0.44	0.78	0.36	0.36
<i>Colloidal clay</i>																	
(ii) Laterite.....	0.3	25.4	26.5	7.1	22.3	1.0	14.0	3.1	(6.04)	2.00	2.46	0.41	0.41
(iii) Pink earth.....	0.1	38.3	9.5	19.1	16.6	0.8	5.0	9.4	(3.41)	0.55	1.22	0.36	0.36
(iv) Red earth.....	3.5	34.1	6.1	28.0	10.5	0.8	3.2	12.4	2.07	0.24	0.82	0.40	0.40
(v) Surface soil.....	1.2	35.8	3.7	29.9	12.5	1.1	2.0	13.6	2.04	0.27	0.79	0.39	0.39
<i>"Ideal" clay-minerals</i>																	
Gibbsite (Al ₂ O ₃ · 3H ₂ O).....													0.33	0.33
Kaolinite (Al ₂ O ₃ · 2SiO ₂ · 2H ₂ O).....													2.00	1.00	0.50	0.50
Halloysite (Al ₂ O ₃ · 2SiO ₂ · 4H ₂ O).....													2.00	0.50	0.25	0.25
Beidellite (Al ₂ O ₃ · 3SiO ₂ · 3H ₂ O).....													3.00	1.00	0.33	0.33
Nontronite (Fe ₂ O ₃ · 4SiO ₂ · 2H ₂ O).....													0.50

* Combined components.

† Expressed as Fe₂O₃ but containing 6.6 per cent TiO₂.

‡ Corrected for organic matter.

a powerful electromagnet, and weighing. In the three sand grades, the remainder was then settled in a solution of potassium mercuric iodide (KHgI_3 ; sp.gr. 2.94) and the proportion of heavy residue estimated by weighing. The identity of the minerals comprising both light and heavy fractions was deter-

TABLE 2
Transformations between parent rock and earthy products
Compositions recalculated to constant total alumina

	PERCENTAGE COMPOSITION					LOSSES OR GAINS			
	(i) Rock	(ii) Lat- erite	(iii) Pink earth	(iv) Red earth	(v) Soil	(ii) Laterite	(iii) Pink earth	(iv) Red earth	(v) Soil
<i>Whole material</i>									
Quartz.....		1.3	0.6	1.6	2.3	+1.3	-0.7	+1.0	+0.7
Combined SiO_2	44.1	7.2	17.5	16.7	20.2	-36.9	+10.3	-0.8	+3.5
Gibbsite.....		11.6	1.6	1.8	1.4	+11.6	-10.0	+0.2	-0.4
Combined Al_2O_3	16.9	5.3	15.3	15.1	15.5	-11.6	+10.0	-0.2	+0.4
Magnetite.....	7.5	6.1	4.9	4.8	4.8	-1.4	-1.2	-0.1	0.0
Amorphous Fe_2O_3	1.8	4.9	4.5	5.9	10.7	+3.1	-0.4	+1.4	+4.8
TiO_2	1.2	1.2	0.6	0.7	1.3	0.0	-0.6	+0.1	+0.7
CaO	14.5	0.6	0.4	0.2	0.3	-21.6	-0.2	+1.0	+0.1
MgO	7.7			1.2	1.7				+0.5
$\text{K}_2\text{O} + \text{Na}_2\text{O}$	4.8								
H_2O									
Gibbsitic.....		6.2	0.8	0.9	0.8	+6.2	-5.4	+0.1	-0.1
Other.....	1.4	2.2	6.0	6.1	7.7	+0.8	+3.8	+0.1	+1.6
Totals.....	99.9	46.6	52.2	55.0	66.7	-53.3	+5.6	+2.8	+11.7
<i>Colloidal clay</i>									
Quartz.....		0.1	0.1	1.7	0.6	+0.1	0.0	+1.6	-1.1
Combined SiO_2	44.1	12.8	22.6	16.9	18.2	-31.3	+9.8	-5.7	+1.3
Gibbsite.....		13.3	5.6	3.0	4.3	+13.3	-7.7	-2.6	+1.3
Combined Al_2O_3	16.9	3.6	11.3	13.9	12.6	-13.3	+7.7	+2.6	-1.3
Fe_2O_3	9.3	11.2	9.8	5.2	6.4	+1.9	-1.4	-4.6	+1.4
TiO_2	1.2	0.5	0.5	0.4	0.6	-0.7	0.0	-0.1	+0.2
H_2O									
Gibbsitic.....		7.0	3.0	1.6	2.2	+7.0	-4.0	-1.4	+0.6
Other.....	1.4	1.6	5.6	6.1	5.7	+0.2	+4.0	+0.5	-0.4
Totals.....	72.9	50.1	58.5	48.8	50.6	-22.8	+8.4	-9.7	+1.8

mined under the microscope by simple optical tests and, in some cases, by dye-stuff tests. The results are presented in table 4. Although the materials show considerable variation in texture (the content of the finer fractions increasing from the laterite to the red earth), the mineralogical composition is remarkably uniform, not only in the different grades, but also in the three

TABLE 3
Transformations between parent rock and earthy products
 Compositions recalculated to kaolinite

		PERCENTAGE COMPOSITION					LOSSES OR GAINS			
		Kao- linite (ideal for- mula)	(ii) Later- ite	(iii) Pink earth	(iv) Red earth	(v) Soil	(ii) Laterite	(iii) Pink earth	(iv) Red earth	(v) Soil
			<i>Whole material</i>							
Nonquartz SiO ₂	46.6	54.0	45.0	43.7	51.2	+7.4	-1.6	-2.9	+4.6	
Combined Al ₂ O ₃	39.4	39.4	39.4	39.4	39.4	
H ₂ O.....	14.0	16.7	15.3	16.0*	19.6*	+2.7	+1.3	+2.0	+5.6	
			<i>Colloidal clay</i>							
(Clay per cent)		10.1	20.1	47.5	50.0)					
Nonquartz SiO ₂	46.6	141.0	79.0	48.0	47.2	+94.4	+32.4	+1.4	+10.3	
Combined Al ₂ O ₃	39.4	39.4	39.4	39.4	39.4	
H ₂ O.....	14.0	17.2	19.4	16.7*	17.8*	+3.2	+5.4	+2.7	+3.8	
			<i>Sand + silt</i>							
Nonquartz SiO ₂	46.6	48.3	39.9	39.4	59.5	+1.7	-6.7	-7.2	-2.4	
Combined Al ₂ O ₃	39.4	39.4	39.4	39.4	39.4	
H ₂ O.....	14.0	16.3	14.7	15.1*	23.2*	+2.3	+0.7	+1.1	+7.9	
<i>Computation as minerals (assuming kaolinite formation)</i>		<i>Whole material</i>					<i>Colloidal clay</i>			
<i>Crystalline components</i>										
Gibbsite.....		38.1	4.6	5.0	3.1	40.5	14.5	9.3	5.7	
Kaolinite.....		28.6	74.3	68.5	56.4	18.0	48.3	70.8	75.6	
Quartz.....		2.8	1.1	2.8	3.3	0.3	0.1	3.5	1.2	
Magnetite.....		12.6	9.0	8.4	6.7	
<i>Amorphous components</i>										
Free iron oxides.....		10.7	8.9	10.9	15.6	22.3	16.6	10.5	12.5	
Free silica.....		2.2	0	0	2.7	17.0	15.8	1.2	0.6	
Titania.....		2.5	1.1	1.3	1.9	1.0	0.8	0.8	1.1	
Bases.....		1.4	0.7	2.5	2.9	
Water (excess).....		0.8	1.1	1.5	3.3	0.6	2.7	2.5	3.1	

*Corrected for organic matter contents.

different profile materials. The bulk of the mineral matter resembles kaolinite in its optical properties.

Dehydration curves

Samples of the fine silt and clay fractions of the laterite, pink earth, and red earth and of gibbsite were exposed to a moist atmosphere in a humidifier con-

taining 50 per cent sulfuric acid in order to bring their initial moisture contents into comparable states. Weighed amounts were then heated in stages to 260°C. in silica weighing bottles in a thermostatically regulated electric oven, and afterward to 800°C. in an electric muffle furnace. The losses in weight for different stages in the heating were determined, and graphs were constructed from the results (fig. 1). Dehydration data for kaolinite, halloysite, and

TABLE 4

Mineralogical composition of red earth profile

Materials washed with boiling acid before mineralogical examination*

	(i) PARENT ROCK	(ii) LATERITE CRUST	(iii) PINK EARTH	(iv) RED EARTH
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
<i>Texture analysis</i>				
Coarse sand.....(>200 μ)	22.3	31.4	18.4
Medium sand.....(200-50 μ)	67.6	28.3	20.5	19.7
Fine sand.....(50-10 μ)	19.8	0.0	17.2	12.3
Coarse silt.....(10-5 μ)	9.7	34.9	0.0	9.0
Fine silt + clay.....(<5 μ)	2.9	14.5	30.9	40.6
<i>Mineral separation (Heavy liquid: sp. gr. 2.94)</i>				
Coarse sand: Magnetite.....	25.3	13.4	24.4
Heavy residue...	0.7	0.0	12.4
Light fraction...	74.0	86.6	63.2
Medium sand: Magnetite.....	7.6	23.2	22.1	23.6
Heavy residue...	18.2	1.1	6.8	12.4
Light fraction...	74.2	75.7	71.1	64.0
Fine sand: Magnetite.....	8.3	1.6	0.0
Heavy residue...	18.0	0.0	0.8
Light fraction...	73.7	98.4	99.2
Notes Heavy residue.....	Augite mainly	Trace of au- gite only	Iron oxide concre- tions mainly	Iron oxide concre- tions
Light fraction.....	Plagioclase felspar mainly	Much kao- linitic mineral	Kaolinitic mineral mainly	Kaolinitic mineral mainly

* Parent rock ground, other profile parts crushed.

beidellite, published by Kelley, Jenny, and Brown (12), were also plotted for comparison on the same diagram.

The curves for the three different materials of the red earth profile show remarkable similarity to the curve for halloysite, although they also show some resemblance to that for kaolinite. The laterite curve is obviously modified by its content of gibbsite.

Physical and chemical soil analysis

Determinations of some constants were made by standard routine methods. The results are set out in table 5. The main features of the profile materials

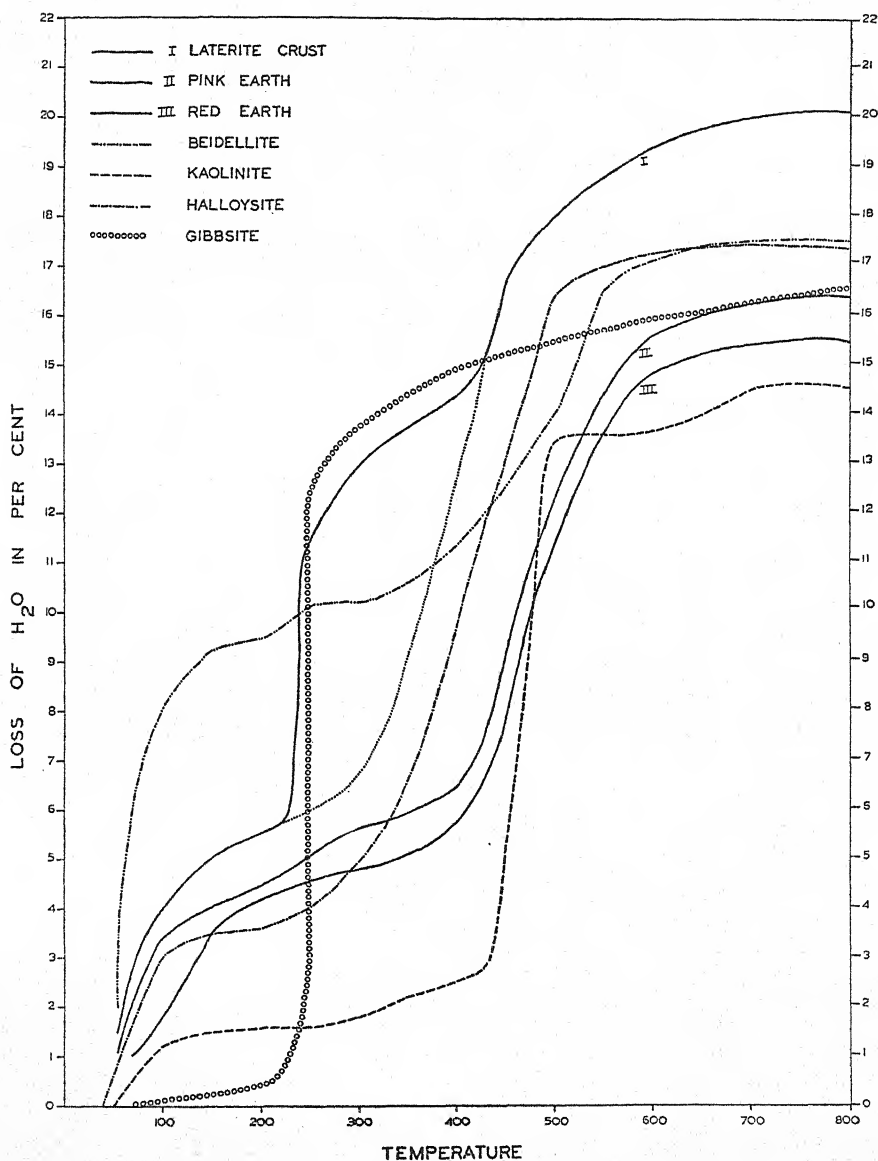


FIG. 1. DEHYDRATION CURVES FOR FINE SILT AND CLAY FRACTIONS OF LATERITE, PINK EARTH, AND RED EARTH PARTS OF PROFILE AND FOR SEVERAL MINERALS

In plotting the gibbsite curve the actual figures obtained for percentage water loss have been halved

are the fair constancy but appreciable magnitude of the values for base-exchange capacity (average, 22.6 m.e.), for sticky point moisture (41.3 per cent), and for residual shrinkage (4.4 per cent), denoting the presence of a mineral resembling halloysite rather than kaolinite. The three layers above the rock are very acid (pH 4.5), but the surface soil is only slightly acid (pH 6.2). Organic matter and nitrogen contents are fairly high in the soil and appreciable in the red earth layer, but negligible below. Available (Truog) phosphate is uniformly low (18 p.p.m.) throughout the profile, and exchangeable potash is medium-low (94 p.p.m.). The soil is not so well supplied with

TABLE 5
Some soil constants of red earth profile

MATERIAL	STICKY POINT MOISTURE	TOTAL SHRINK- AGE	RESIDUAL SHRINKAGE	BASE EXCHANGE CAPACITY	REACTION	TOTAL ORGANIC MATTER	TOTAL NITROGEN	C/N RATIO	AVAILABLE P ₂ O ₅ (TRUOG)	AVAILABLE (EXCH.) K ₂ O
	<i>per cent</i>	<i>per cent</i> *	<i>per cent</i> *	<i>m.e.</i>	<i>pH</i>	<i>per cent</i>	<i>per cent</i>		<i>p.p.m.</i>	<i>p.p.m.</i>
(v) Soil.....	41.3	6.2	4.0	0.22	10.8	22	92
(iv) Red earth.....	42.0	46.1	4.3	24.4	4.4	1.1	0.06	10.8	13	..
(iii) Pink earth.....	41.6	24.8	4.5	21.3	4.3	0.3	0.02	9.3	16	96
(ii) Laterite.....	40.4	22.2	4.7	0.1	0.01	7.3	21	60
(i) Rock.....	7.9	66	..

* Of dry volume.

nutrients, particularly potash, as are the majority of the Grenada red soils which regularly yield good crops of cacao (8).

Dye tests

Alizarin adsorption for determining gibbsitic alumina was measured by a modification of the earlier method (5), which involves the use of an electric furnace rather than uncontrolled heating in crucibles over open burners (*see* appendix). The alizarin-stained *ignited* material is thoroughly washed with hot water rather than boric alcohol before stripping with oxalate solution. The alizarin dye-standard is made up with a blank oxalate extract of the ignited material, rather than pure oxalate solution; this accurately compensates for ferrioxalate ion, which imparts an undesirable green color, so that no blue dye need now be added to the color standard. With these improvements, the alizarin method is considered to be reliable and quantitatively precise. On the other hand, its value for estimating hydrous iron oxides in *unignited* fresh materials still remains doubtful, since certain clay minerals (for example, halloysite and beidellite) have been found capable also of adsorbing alizarin before ignition (*see* table 6).

The adsorption of dyes other than alizarin was examined as a possible means

TABLE 6

Comparative dye tests on standard materials and red earth profile samples

Values in dye units absorbed per gram of air-dry material

MATERIALS*	LOSS ON IGNI- TION	ALIZARIN UPTAKE	DIAMINE SKY BLUE UPTAKE			JANUS RED UPTAKE
			Boric	Phos- phatic	Difference	
	<i>per cent</i>					
<i>Authentic minerals</i>						
1. "New" aluminum hydroxide...	44.9	1250 (2273)†	1112 (2018)	12 (22)	1100 (1996)	10
2. "Aged" aluminum hydroxide...	55.2	665 (1486)	76 (170)	82 (183)	0 (0)	18
3. Gibbsite bauxite.....	33.1	4 (6)	93 (150)	6
4. Ferric hydroxide.....	44.8	1375 (2490)	2544 (4610)	0 (0)	2544 (4610)	6
5. Turgite.....	17.0	168 (213)	328 (416)	0 (0)	328 (416)	20
6. Limonite.....	10.8	38 (46)	46 (56)	47
7. Kaolinite.....	12.8	15	52 (60)	50 (57)	2 (3)	340
8. Halloysite.....	17.2	148	667 (805)	517 (624)	150 (181)	1240
9. Beidellite.....	20.6	93	80 (101)	982
10. Montmorillonite.....	19.2	11	31 (38)	30 (37)	1 (1)	2000
<i>Profile samples—whole material</i>						
(i) Parent rock.....	1.4	21	30 (31)	25 (25)	0† (0)	83
(ii) Laterite.....	18.0	99	390 (473)	83 (100)	282† (344)	704
(iii) Pink earth.....	13.0	147	574 (644)	246 (286)	254† (292)	1298
(iv) Red earth.....	12.7	143	482 (552)	85 (97)	371† (425)	1096
(v) Soil.....	12.2	107	60 (69)	40 (45)	8† (9)	1056
<i>Profile samples—colloidal clay</i>						
(ii) Laterite clay.....	17.1	1040 (1250)	310 (370)	668† (806)	790
(iii) Pink earth clay.....	14.4	815 (950)	465 (545)	257† (300)	2365

* All materials previously air-dried, but *not* ignited, and ground to pass 100-mesh sieve.

† Figures in parentheses are dye values recalculated to ignited basis.

‡ Dye values corrected for dye uptake by phosphated halloysite.

TABLE 6—*Concluded**Sources of minerals:*

- 1, 2, 4. *Laboratory preparations*; precipitation from solutions of metal-chloride by ammonium hydroxide at 0°C. "Aged" alumina, stored for 8 years.
3. *Gibbsitic bauxite*; Demerara Bauxite Co., high-grade ore. Contains 62 per cent Al_2O_3 and 33 per cent H_2O .
5. *Turgite*; Gregory, London. Contains 79 per cent Fe_2O_3 and 17 per cent H_2O .
6. *Limonite*; Eimer and Amend, New York. Contains 82 per cent Fe_2O_3 and 11 per cent water.
7. *Kaolinite*; Baird and Tatlock, London. Commercial sample.
8. *Halloysite*; Lawrence, Missouri. Presented by Dr. C. E. Marshall.
9. *Beidellite*; Clay fraction of Putnam clay. Presented by Dr. C. E. Marshall.
10. *Montmorillonite*; Clay fraction of Volclay. Presented by American Colloid Co. by request of Dr. C. E. Marshall.

of identifying and approximately estimating specific clay minerals as well as hydrous iron oxides. Some 30 different dyes were tried, including examples of basic and acidic classes, but only two—diamine sky blue and janus red—have so far proved useful. The methods of applying them are given in the appendix. The results obtained by dye tests, both for standard minerals and for red earth profile samples, are set out in table 6.

RESULTS

Laterite formation

The analytical data in tables 1 and 2 clearly demonstrate the nature of the profound alterations that affect the parent rock, changing it into primary laterite. Assuming no loss in total alumina, the chief results are (a) the liberation and removal of nearly all the bases (potash, soda, lime, magnesia), (b) the liberation of combined silica, much of which is evidently transported upward into the layer above, though a little crystallizes as secondary quartz, most of the remainder being lost, (c) the liberation and crystallization as gibbsite of a large part of the combined alumina, (d) the change of some of the magnetite into hydrous iron oxide, (e) the formation of hydrous iron oxide by the hydrolysis of the ferromagnesian minerals, (f) the absorption of a considerable quantity of water, part of which is fixed in new crystalline minerals, and part in colloidal hydrous oxides. These transformations are very similar to those described by Harrison (9) and by Hardy and Follett-Smith (7) as affecting basic igneous rocks in British Guiana.

The total loss of oxide components (mainly silica and bases) by the decomposing parent rock in the Grenada profile amounts to over 60 per cent, and the first product (primary laterite) is distinguished by the occurrence of the unique secondary mineral, gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), comprising nearly 70 per cent of its total alumina content.

The remainder of the alumina, assuming no removal, has presumably combined with part of the liberated silica to form some new aluminosiliceous mineral, the identity of which needs to be determined now. The evidence sup-

plied by chemical analysis alone is not sufficient for complete identification, but information provided by mineralogical examination, by physical constants, and particularly by the striking dehydration curves, proves beyond doubt that it is a mineral of the kaolin class, resembling halloysite in most of its properties, although its content of constitutional water falls short of the requirement of the formula, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, rather suggesting *metahalloysite*, $(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O})$ (14). Assuming the formula for metahalloysite, the computations show that the primary laterite contains about 38 per cent gibbsite, 29 per cent metahalloysite, 13 per cent magnetite, and 3 per cent secondary quartz, a total of 83 per cent crystalline components. The residue is apparently made up of $2\frac{1}{2}$ per cent titania, 1 per cent bases, 1 per cent combined water, $10\frac{1}{2}$ per cent free iron oxide, and 2 per cent silica. The occurrence in the laterite of unaccounted and presumably free silica other than quartz is significant, and the analytical data prove that it is confined almost entirely to the colloidal clay fraction (table 3). This fraction, comprising 10 per cent of the whole material, apparently contains no less than 17 per cent unaccounted silica not quartz, if metahalloysite is assumed to be the only aluminosiliceous mineral present. As there is no evidence that this surplus silica occurs in any other combination (such as anauxite, allophane, pyrophyllite, or nontronite), it may be regarded as amorphous or colloidal silica that has been liberated but not removed. It may comprise the chief cementing agent that confers brittleness on the coherent laterite crusts.

The hydrous iron oxide residues, other than those derived from magnetite, have remained as pseudomorphs of the augite phenocrysts² and have not migrated perceptibly into the groundmass of the laterite.

Pink earth formation

The layer above the laterite crusts covering decomposing basic igneous rock, and presumably derived from it, is remarkable for the fact that its content of gibbsite is very much less and its content of combined alumina is correspondingly greater than that of the laterite.³

² Analyses of porphyritic augite crystals isolated from the Grenada augite-andesite recorded by Harrison (10) show: SiO_2 , 46.8; Al_2O_3 , 8.8; Fe_2O_3 , 10.5; CaO , 20.9; MgO , 13.3 per cent (total 100.3). Hence the partition of the oxide components in the augite contained in the parent rock (15.5 per cent) should be, SiO_2 , 7.3; Al_2O_3 , 1.4; Fe_2O_3 , 1.7; CaO , 3.2; MgO , 2.1 per cent, leaving SiO_2 , 36.8; Al_2O_3 , 15.5; Fe_2O_3 , 0.1; CaO , 11.3; MgO , 5.6 per cent to be shared between plagioclase feldspars and olivine. As the small residue (0.1) of Fe_2O_3 implies that the olivine is a magnesian and not a ferric type (i.e. forsterite), most of the iron oxide residues resulting from the weathering of this rock are derived from its augite component, thus explaining the relatively pale color of the groundmass of the laterite crust and of the pink earth.

³ Harrison (9) explains this striking feature by supposing that *resilication* of gibbsite proceeds in the upper part of the laterite layer as a result of the upward movement of ground-water carrying colloidal silica or alkali silicates in solution. He further supposes that this rising of ground water occurs by capillarity during dry seasons at sites where the drainage is impeded. Harrison assumes that, under conditions of free drainage, no resilication proceeds, but instead, the primary laterite accumulates in increasing thicknesses.

The product of gibbsite silication is believed to be some *kaolin* mineral, and the analytical data, augmented by other evidence presented in the tables and the dehydration graphs, support this conclusion in the case of the Grenada profile and suggest further that it is metahalloysite, as in the laterite. An appreciable residue (16 per cent) of uncombined silica remains in the clay fraction of the pink earth (table 3), as in the laterite, although it is absent from the overlying red earth.

The pink earth contains 74 per cent metahalloysite, 5 per cent gibbsite, 9 per cent magnetite, and 1 per cent quartz, a total of 89 per cent crystalline components. The amorphous residue consists mainly of 9 per cent free iron oxide (presumably hydrated by the 1 per cent unaccounted combined water), which is very unevenly distributed within the gray-white kaolinitic clay and still exhibits marked segregation as augite pseudomorphs. The pink earth evidently comprises an *active zone of secondary changes*, and represents a transition between gibbsitic laterite and red earth proper.

Red earth formation

The red earth layer is a homogeneous mass apparently consisting chiefly of metahalloysite ($68\frac{1}{2}$ per cent), stained uniformly red by hydrous ferric oxide ($10\frac{1}{2}$ per cent), together with 5 per cent gibbsite, 9 per cent magnetite, and 3 per cent secondary quartz. The composition of its colloidal clay component, comprising about 50 per cent of the whole, is almost identical with that of the rest of the material, a noteworthy feature of the red earth. Furthermore, the clay contains no excess of free colloidal silica, the resilication of gibbsite evidently having proceeded as far as possible at the base of the layer. The red earth proper may thus be regarded as a *zone of completed secondary changes*.

As organic matter occurs in appreciable quantity (1.1 per cent; see table 5) in the red earth layer, it evidently comprises part of the solum. Plant roots occur throughout its depth, some even penetrating the pink earth below and reaching the laterite-encrusted boulders where these are not too deep-seated. The mineralization of the organic matter may account for the somewhat greater content of bases in the red earth as compared with the underlying pink earth.

Surface soil formation

The uppermost layer of the Grenada profile differs only slightly in appearance from the layer below, which it closely resembles in chemical and mineralogical composition. Its crystalline components consist of 56 per cent metahalloysite, 3 per cent gibbsite, 3 per cent quartz, and 7 per cent magnetite; its amorphous part, amounting to 30 per cent of the whole, mainly comprises hydrous iron oxide ($15\frac{1}{2}$ per cent). It contains more total bases and constitutional water than does the red earth layer, and it shows a relatively higher content of titania, considered to be a characteristic feature of the A horizon of lateritic types of soil as contrasted with podzolic types (11). The

clay fraction of the soil includes a higher proportion of kaolinitic mineral than the sand and silt, but less free quartz.

These results do not demonstrate the effects of profound leaching (tropical podzolization), such as prevails in British Guiana where red earths usually exhibit bleached sandy surface layers, consisting almost entirely of white residual quartz. Nowhere in Grenada is such highly leached degraded red earth to be found, the soils instead appear to be somewhat immature, and in certain cases, the composition of their surface layers has apparently been modified by a covering of geologically recent volcanic ash derived within the island itself or from some neighboring island.

DISCUSSION

Primary laterization

Primary laterization appears to be a fundamental process, apparently dependent on the conditions of weathering⁴ as well as on the chemical or mineralogical composition of the parent rock.⁵ Abundant evidence may be adduced in support of the view that acidic igneous rocks, rich in 6-silica feldspars, microcline, and quartz, when hydrolyzed, liberate such large quantities of reactive silica (colloidal silica or silicate ion), that alumina molecules immediately on liberation, are silicated into a secondary kaolinitic mineral or even sericite mica, free alumina seldom appearing among the end products. On the other hand, basic igneous rocks, containing 2-silica feldspars (lime feldspars) and little or no quartz, liberate much lesser amounts of reactive silica in proportion to alumina, and consequently, in accordance with the laws of mass action, much lesser amounts of kaolinitic products appear, the excess of free alumina crystallizing out as gibbsite. Presumably the formation and accumulation of gibbsite would be enhanced by free drainage, because this favors the rapid removal of silica in solution. Harrison repeatedly stresses the importance of free drainage in primary laterization, and it is generally agreed that kaolinization proceeds best under poor drainage conditions.

Silication of gibbsite

The resilication theory, as postulated by Harrison (9), would probably not be accepted by physical chemists, although the essential facts now appear to be demonstrable. The conditions favoring the process have not been specifically investigated, but merely conjectured. Resilication necessitates, first, the provision of an abundant and continuous supply of silica or silicate ion in solution and, secondly, its transportation to and precipitation within the mass of gibbsite-containing laterite. The coincidence of these two circumstances would appear to be rare, since the greatest amount of silica is liberated through mineral hydrolysis during the wet season when the rainfall is continuous and heavy and when water is con-

⁴ For example, Mattson (16) regards laterization as essentially a mineral hydrolysis proceeding under alkaline conditions.

⁵ De Sigmund (19, p. 29) refers to his researches on artificial zeolites, by which he demonstrated that "in an alkaline medium, Al_2O_3 is usually precipitated together with a part of the silicic acid and with some of the bases, while the rest of the silicic acid and bases remains in solution and may be leached out. This occurs during the weathering of natural silicates in pure water. In an acid medium, different conditions prevail." He also (19, p. 23) cites Harrassowitz in support of the view that, "whereas in orthoclase, kaolin may really be formed, the products resulting from calcium and sodium feldspars are allophanoids" (that is, mutual solutions of silica, alumina, and water, easily dissolved by hydrochloric acid, and colloidal in form).

stantly moving *downward*, whereas the process of resilication presumably necessitates, according to Harrison, *upward* movement of ground water. Harrison assumes that this occurs as a result of capillary action during the dry season. Actually, at this period, there may be an insufficiency of colloidal silica to effect resilication, because most of the silica-bearing water may already have drained away.

It is possible, however, to explain gibbsite silication in another way, namely, by taking into account the effects of *dilution* of the concentrated solution of colloidal silica by *descending* water that has penetrated the soil as rain.⁶ This water has already traversed a highly acidic layer of red earth before intermingling with the solution of silica; its reaction, therefore, is probably acidic. Furthermore, mere dilution has been shown by Buehrer and Williams (2) greatly to reduce the alkalinity of mixtures of finely divided feldspars and pure water, although no explanation is offered of the phenomenon. Thus, in the case of albite, a decrease in pH value from 9.5 to 6.2 was observed for a change in feldspar-water ratio of 1:2 to 1:100.

The new theory may be stated as follows: We may first assume that the laterite layer is impregnated from below with a concentrated alkaline solution of colloidal silica throughout the wet season, and that excess of solution is continually draining away over the decomposing rock surface. We may further assume that the level of saturation falls rapidly in the intervals between rainy spells, and during these spells the upper part of the solution is subjected to dilution by descending acidic water. Under these circumstances, silica will be precipitated around the gibbsitic nuclei occurring in the upper part of the laterite layer. The marked change in reaction conditions in this part of the profile will favor the mutual adsorption of alumina and silica, for, according to the isoelectric theory as postulated by Mattson (16), the alumina particles will acquire electropositive charges when the reaction becomes more acidic than the isoelectric point of alumina (stated variously to range from pH 6.5 to 8.1), whereas the silica particles will be electronegatively charged, having an isoelectric point very low on the pH scale. By slow degrees, the coprecipitate will become stabilized through irreversible dehydration, favored especially by the onset of the dry season when the water table sinks to the level of the parent rock. It will slowly "age," passing through stages such as allophane, until it eventually crystallizes as a kaolinitic mineral, probably halloysite.

It seems likely, therefore, that both primary laterization and resilication occur across narrow boundary zones, and that reaction conditions, as well as degree of wetness and solute concentration, may fluctuate constantly between wide limits, setting up reversible gradients alternately favoring the one process and then the other.

The mechanism of laterization and gibbsite silication may be complicated in some instances by changes in ground-water conditions consequent on a lowering of base levels of erosion by tectonic uplift, which may result in a rejuvenation of the drainage.⁷ Such changes might favor laterization rather than kaolinization; consequently, a zone of primary laterization displayed at the present time in a red earth profile may merely represent a comparatively recent development. A historic sequence of topographical events similar to this actually appears to have affected the hinterland of British Guiana during late Pleistocene times, and evidence is afforded by the occurrence of high-level limestones that Grenada also was elevated above the sea during the same geological period. On the other hand, red earth derived from basalt in South Carolina (Davidson clay loam)⁸ has been proved by the writers to exhibit very similar features to those of the Grenada soil, clearly showing a transition between primary gibbsitic laterite and kaolinitic red earth. Whether the incidence of successive phases

⁶ The writers are indebted to Irvin C. Brown, of the U. S. Bureau of Soils, for this suggestion, communicated by G. Milne.

⁷ G. Milne, private communication.

⁸ The writers are indebted to J. F. Lutz, of the North Carolina State College of Agriculture, for providing profile samples of the Davidson red earth, including laterite crusts on basalt boulders.

of a changing set of geological conditions must be invoked to explain the development of red earth in the southeastern United States, as well as in the other two areas, could only be decided by further intensive investigations.

Redistribution of iron oxide in the pink earth layer

The most striking difference between the red earth and the pink earth is its uniform bright coloration, as contrasted with the orange-mottled, fine red-speckled, and patched bluish-gray appearance of the pink earth. This cannot be accounted for by a difference in gross composition; it is apparently solely due to a more uniform distribution of the iron oxide component in the red earth. Possibly iron occurs in the pink earth partly in the ferrous state, generally believed to be more mobile than ferric iron. The constant wetness of the material would be conducive to the maintenance of temporary reducing conditions, under which some of the iron compounds would exhibit bluish colorations. During upward diffusion into a drier zone, rapid oxidation of iron and the partial dehydration and agglomeration of its hydrous oxide products might produce a stable red mineral resembling goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) or a mixture of goethite and hematite (Fe_2O_3). Whether the diffusion or migration of the hydrous ferric oxides is aided by colloidal silica (the occurrence of which in the pink earth is indicated by the chemical analyses) in accordance with the theory of Riefenberg (17), or by some other agency such as humus, can only be conjectured as possibilities. Whereas the pink earth may be regarded as a zone of intermittent saturation within which active secondary changes proceed, the red earth layer may be considered to be a zone of non-saturation where these changes are completed and where equalization, fixation, and thorough oxidation of the iron oxide component are effected. The red earth is the end product of this sequence of mineralogical transformations; to the pedologist it would therefore comprise the parent material from which a fertile soil might be produced by the cooperation of biotic factors.

Identity and properties of the iron oxide component

The most characteristic and interesting component of the red earth profile is hydrous iron oxide, the properties of which probably affect greatly the agricultural behavior of the soil when cropped, as well as its response to manuring. Its main feature appears to be a high specific adsorptive capacity for acidic radicals or colloidal anions, as revealed, for example, by its pronounced uptake of acidic dyes such as diamine sky blue (table 6). For purposes of comparison, dye values for various specimens of alumina, iron oxide, and clay minerals were determined. The results show that the more highly hydrated iron oxides and fresh aluminum hydroxide strongly adsorb alizarin and diamine sky blue from their solutions in boric alcohol, though these dyes are also appreciably adsorbed by halloysite, only slightly by beidellite, and scarcely at all by gibbsite, kaolinite, and montmorillonite. In the presence of phosphate, however, hydrous iron oxides and aluminum hydroxide no longer adsorb diamine sky blue (a blocking effect by phosphate), but halloysite and beidellite still adsorb it, showing a diminution of only 30 per cent in dye value. On the other hand, hydrous iron oxides and aluminum hydroxide do not appreciably adsorb janus red (a basic dye), nor does gibbsite, but still the clay minerals adsorb it very strongly, kaolinite least, and montmorillonite most. Unfortunately, the magnitudes of the dye values cannot be regarded as quantitatively significant, because they depend on several uncontrolled variable factors, notably particle size, degree of hydration, and state of agglomeration. Partly for this reason, no attempt will be made to interpret the results for the profile layers except in a general way.

From the diamine sky blue data in table 6, it will be noted that the material of each of the layers except the surface soil apparently contains considerable amounts of free iron oxide. The average dye value, per gram Fe_2O_3 , is 3,570 units, which further suggests that this component is an extremely active adsorbent, resembling the artificial preparation of ferric hydroxide (4,610 units per gram Fe_2O_3) rather than either of the specific minerals, turgite and

limonite. This finding agrees with the results of the previous investigation of iron oxide minerals by the original alizarin method (7).

The iron oxide component of the surface soil, although greater in quantity than that of the layers below, is evidently very much less reactive, its dye value, per gram Fe_2O_3 , being only 60 units. This may imply a much lower degree of hydration (insofar as hydration may partly decide the absorbing capacity of hydrous iron oxides for acidic dyes), indicating the pronounced surface drying to which the soil is subjected during dry seasons.

From the results of the janus red tests, it will be seen that the material of each layer contains large amounts of a reactive aluminosiliceous mineral. The average dye value, per gram kaolinitic mineral present, is 1,925 units, which is greatly in excess of the value for the specimen of kaolinite, but of the same order as that for halloysite, the presence of which has been conjectured on other evidence. Data for the clay fractions of the laterite and the pink earth, however, give an average janus red dye value, per gram of presumed kaolinitic mineral, of 4,650 units, which is considerably higher than that given by any of the minerals examined. This abnormality perhaps may be explained by the supposition that these two layers contain free colloidal silica, though this is scarcely supported by the results of the Truog treatment next to be described.

Truog treatment

As a further test of the nature of the reactive components of the laterite and the pink earth, samples of the materials were examined by the Truog procedure for "removal of free iron oxide, free alumina and colloidal silica" (20), by treatment with sodium sulfide and oxalic acid under alternating alkaline and acidic conditions. The results obtained by chemical analysis of the extracts, and dye values for the residual materials after treatment, are presented in tables 7 and 8. They further demonstrate that the iron oxide component is uncombined, being almost completely removable by the treatment, leaving colorless residues. Some, though not all, of the gibbsitic alumina in the laterite and most of that in the pink earth are dissolved by the treatment. Only a small proportion of the total silica is removed, though apparently not solely the free colloidal silica, and the activity of the aluminosiliceous minerals, as measured by the adsorption of janus red, seems to have been considerably increased by the treatment which possibly enhances their dispersion.

Phosphate fixation

The agricultural importance of free active hydrous iron oxide in soils lies in the ability of this oxide to adsorb and to fix a large amount of phosphate ion (for example, from added soluble manures), which becomes available to plants only under special circumstances (19). In order to examine the phosphate-fixing ability of the Grenada red earth, Beater's method (1) was applied to samples of the four profile materials, as well as to the artificial ferric hydroxide preparation. The results showed that the materials are capable of adsorbing from neutral ammonium phosphate solutions between 6.8 and 14.4 m.e. of phosphate ion per 100 gm., the surface soil adsorbing least, and the laterite layer most, while the laboratory preparation of ferric hydroxide adsorbed 16.8 m.e. The surface soil, though least active, is nevertheless capable of fixing about 0.163 per cent of its weight of P_2O_5 , or 1,630 p.p.m. P_2O_5 . From acidic solutions (pH 3.5) each material further adsorbed about 25 per cent additional phosphate.

CONCLUSIONS

Determination and significance of silica-sesquioxide and hydration ratios

Silica-sesquioxide ratios have been increasingly employed in recent years for assessing the degree of mineral decomposition of rocks and the extent of degradation by leaching of the products of weathering during the subsequent development of soil profiles from the derived parent materials. They have also been applied in attempts to define the terms "laterite" and "lateritic,"

and for distinguishing different types of clay. In view of the fact that certain secondary clay minerals, notably beidellite and montmorillonite, may apparently suffer substitutions of aluminum for silicon and of magnesium and iron for aluminum in the lattice layers (14), great variation in the silica-sesquioxide ratio may be expected, particularly for *sedimentary rocks* that contain specific clay minerals in abundance. Such variation will have no genetic or pedologic significance in these cases. On the other hand, the ratio may have considerable significance in the case of rock products containing primary min-

TABLE 7

Components removed by Truog treatment
Values in percentages of original whole material

MATERIAL*	COMPONENTS REMOVED BY TRUOG TREATMENT			ORIGINAL COMPONENTS				
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Free SiO ₂	Com- bined SiO ₂	Gibbsitic Al ₂ O ₃	Com- bined Al ₂ O ₃	Free hydrous Fe ₂ O ₃
Laterite.....	0.7	5.4	8.4	2.2	15.5	24.9	11.3	10.4
Pink earth.....	0.8	3.0	8.0	0	33.5	3.0	29.3	8.6

* 100-mesh.

TABLE 8

Dye values for residual materials after Truog treatment
Values in dye units per gram of original whole material

RESIDUAL MATERIAL	BEFORE TREATMENT					AFTER TREATMENT				
	Aliz- arin*	Diamine sky blue			Janus red	Aliz- arin*	Diamine sky blue			Janus red
		Boric	Phos- phatic	Differ- ence			Boric	Phos- phatic	Differ- ence	
Laterite.....	249	390	83	282	704	192	100	0	100	1304
Pink earth.....	30	474	246	254	1298	20	428	236	113	1860

* Ignited material.

erals belonging to the kaolin group or consisting of simple mixtures of sesquioxides and silica commonly resulting from the weathering of *igneous rocks* in the humid tropics. Here the determination of the individual free sesquioxides and silica may help considerably in the complete definition of these products.

Free silica in the form of quartz may now be determined with considerable accuracy in rock-weathering products by the tri-acid digestion method (7), and in this way it may be distinguished from silica combined in aluminosilicates and ferrosilicates. *Free alumina* likewise may be estimated by the improved alizarin method applied to the *ignited* material, for it is the only component whose capacity for adsorbing alizarin is not greatly diminished by intense heat. Unfortunately, this property applies to amorphous or colloidal alumina as well as to crystalline gibbsite, and it therefore cannot be used for distinguishing between them. Studies of bauxites, bauxitic clays, and laterites

have indicated, however, that free alumina generally occurs naturally as gibbsite, at least in humid tropical rock-weathering products (9). This fact may not preclude the possibility of its occurring in the amorphous form in certain materials such as alkali subsoils, although direct demonstration would be difficult, except by the application of some specific test, and none seems yet to have been elaborated. *Free iron oxide*, in the form of magnetite, where present, may easily be removed and determined directly by weighing.

The advantages of this new departure from the conventional method of expressing the results of chemical analysis of weathering products are revealed by the ratio values given in table 1, which confirm the identity of the halloysitic component of the four kinds of materials comprising the Grenada red earth. Were it not for the fact that quartzose silica, gibbsitic alumina, and magnetic iron oxide could be eliminated by the methods employed, the computation of the probable mineralogical composition of the four layers of the profile would have been impossible. Furthermore, the value of mineralogical determinations, thermal analysis, and measurements of soil constants, as a check on the computations, is clearly demonstrated. Unfortunately, the dye tests as applied to the fresh materials have failed to assess the various iron oxides, although they have indicated their high degree of activity and their ability to combine with considerable amounts of phosphate. The use of similar but more sensitive dyes and of a greater range of authentic reference minerals, together with further improvements in technic, such as the strict standardization of particle size by centrifugal fractionation, would increase the selectivity and precision of the dye tests and is worthy of further study.

Classification of parent materials of red soils

The application of the procedures described and illustrated in this article should materially help in classifying humid tropical and subtropical soils (6), and particularly in further subdividing so-called laterite and lateritic types. In this connection, the writers agree with the view expressed by Marbut (13) that "laterite is a geological material . . . from which more than one type or group of soils may develop"; it may either give rise directly to a red soil (laterite soil), or it may first produce red earth by resilication (as in the case of the Grenada profile), which may then become the parent material of other kinds of red soil, certain of which may be lateritic.

Mineralogically and chemically, the name *laterite* in soil literature has come to mean a rock-product characteristically rich in gibbsite, although other minerals and amorphous substances may also occur in it, such as kaolins (mainly halloysite), hydrous iron oxides, primary and secondary quartz, colloidal silica, manganese oxide, and titania. Alkalies and alkaline earths are typically absent. When iron is especially abundant in the original rock, iron oxide usually accumulates as concretions and crusts or as vesicular slaggy masses, many of which are indurated. The silica-alumina molecular ratio of such a gibbsitic material would be considerably less than 2.0 (the ratio for kaolins), and this fact has given rise to the modern pedologic conception of

laterite as essentially an aluminous material having a silica-alumina ratio less than that of kaolin minerals. Thus, according to Scrivenor (18), "a few analyses have destroyed the value of laterite as a scientific term," because the name originally was given to an Indian building stone having certain characteristic features, such as hardening on exposure, though a low silica-alumina ratio was not among them, as has been proved recently by the examination of authentic specimens (4).

In view of the fact that the mineralogical composition of laterite cannot be determined by conventional chemical analyses, which allow no differentiation between free and combined silica and alumina, recourse must be had to other methods such as those described in this article. By the application of these methods the parent materials of red soils may now be exactly described and defined on the basis of their content of gibbsite, kaolins, and free iron oxides, as well as that of other less essential components. As a beginning, it is tentatively suggested that the parent soil materials might be classified, first, on their gross contents of gibbsite⁹ into (a) those that contain much gibbsite (for example, over 20 per cent¹⁰ of their weight), namely, *bauxites* and *laterites*, and (b) those that contain little or none, namely, *primary kaolinic clays*. The materials belonging to each class might then be subdivided on their contents of kaolin minerals, and those belonging to each of these subclasses might be subdivided again on their contents of iron oxide. The proposed provisional nomenclature may be represented schematically as follows:

GIBBSITE ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)	KAOLINS ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$)	IRON OXIDE ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$)	PROPOSED NAME
(a) <i>Gibbsitic class (bauxites and laterites)</i>			
Much*.....	Much*	Much* Little	(i) Kaolinic laterites (ii) Bauxitic clays
	Little	Much Little	(iii) Laterites; ferruginous laterites (iv) Bauxites (high grade)
(b) <i>Kaolinic class (primary clays)</i>			
Little.....	Much	Much Little	(i) Ferruginous kaolinic clays (ii) Kaolinic clays (white)
	Little	Much Little	(iii) Ferruginous clays (iv) (Quartzites, manganese ores, etc.)

* By "much" is implied more than 20 per cent by weight.

⁹ Fermor (3) proposed to differentiate between laterites and lithomargic clays (amorphous kaolinic or allophanic clays) on the basis of content of "lateritic components," namely, hydrates of alumina, ferric oxide, and titania.

¹⁰ Corresponding to alizarin dye values per gram material after ignition, of 125 units up to 624, the value for pure gibbsite.

The gibbsitic class of rock products presumably includes materials derived from basic and intermediate igneous and metamorphic rocks, whereas the kaolinic class includes china clays, pipe clays, and pot clays mostly derived from acidic rocks such as granite, often stained to different degrees by hydrous iron oxides. This class would also include highly ferruginous products derived from ultra basic rocks (peridotite; serpentine), such as Nipe clay, of Cuba and Puerto Rico. When quartz is plentiful in addition, the descriptive prefix, quartzose, might be employed, and when manganese oxide is abundant, the prefix, manganiferous, might be used.

According to this classification, *laterite* (in the pedologic sense) would be defined as a parent soil material ranging from pure bauxite (or gibbsitic rock; Al_2O_3 , 65 per cent), to a material containing not less than 20 per cent gibbsite or more than 50 per cent kaolins, with 30 per cent hydrous iron oxides, or with 30 per cent of a mixture of iron oxides, quartz, colloidal silica, and other accessory components. The material representing the lower end of this laterite range would thus have a combined silica content of about 25 per cent, and a total alumina content of about 33 per cent (13 per cent of it being free), giving a silica-alumina molecular ratio below 1.33, which conforms with the standard suggested by Martin and Doyne (15).

With decreasing content of gibbsite and increasing content of kaolins, the material might still be described as *lateritic*, but when the content of gibbsite has diminished to zero, it could no longer be described thus, but should be named *kaolinic clay*, with appropriate prefix denoting the presence of other products. The general terms *red earth* (or *lateritic red loam*) and *red loam* would be equivalent to the terms *ferruginous lateritic clay* and *ferruginous kaolinic clay*, and the term *terra rossa* might be retained for further describing these materials when they accumulate over hard limestones. If, in addition, the type and degree of adsorptive activity of the iron oxide component of ferruginous clays were to be indicated from the results of improved dye tests (for example, by the substitute prefixes *turgitic*, *limonitic*, *hematitic*, etc., these terms having first been standardized), then further definition could be given to the different products of primary rock weathering, and eventually a comprehensive classification of the derived parent soil materials could be elaborated.

In recent years, a tendency has developed for grouping together all red-colored parent soil materials for the purpose of defining soil series, no matter what their origin or mode of formation. Though praiseworthy insofar as it simplifies soil classification, the practice should not be permitted to spread unduly, since it should now be possible to describe and define the parent soil materials in terms other than those of mere coloration and structure. At least in theory, the classification of parent soil materials in all cases should be based on their entire mineralogical composition. In attaining this end, the employment of laboratory methods other than chemical analysis should prove valuable, provided such methods are sufficiently simple and reliable for

routine application. It is hoped that some of the methods described in this article may meet these requirements.

SUMMARY

The main object of the work described in this paper was to investigate various laboratory methods for following the transformations of a basic igneous rock into the parent material of a red soil, and the genesis of soil from it.

The methods used were chemical analysis of whole materials and colloidal clay components, mineralogical examination under the microscope, the construction of mineral dehydration curves, the determination of some physical and chemical soil constants, and dye adsorption tests, including an improved alizarin test for gibbsite and some other tests (diamine sky blue and janus red) for hydrous iron oxides and clay minerals.

These methods were applied to representative materials obtained from a deep red earth profile overlying augite andesite as developed in Grenada, British West Indies, under a humid tropical climate with pronounced wet and dry seasons.

It was found possible by the application of these methods to distinguish and to determine quartzose silica and combined silica, free (gibbsitic) alumina and combined alumina, magnetite, and hydrous iron oxides. The separate determination of the free oxides made it possible to estimate the amounts of secondary aluminosiliceous minerals present in the several materials, and so revealed their identity as kaolins (probably metahalloysite chiefly, with some kaolinite).

The formation of primary laterite from the parent igneous rock and of pink earth and red earth from the laterite is described and discussed. The red earth may be regarded as the parent material of the surface soil, but as no very marked soil development has occurred in this case, the discussion mainly concerns the processes of laterization, gibbsite silication, and the redistribution of iron oxide.

A new theory to account for gibbsite silication as an essential process in the transformation of primary gibbsitic laterite into *secondary* kaolinic red earth is submitted, based on colloid chemical interactions between descending acidic water and alkaline silica solutions comprising ground water the level of which fluctuates within the zone of intermittent saturation coinciding with the pink earth layer. The formation of red earth from pink earth involves no further changes other than the redistribution of hydrous iron oxides, their completed oxidation, partial dehydration, and equalization.

In view of the great agricultural importance of the phosphate relations of ferruginous soils, the adsorptive properties of the hydrous iron oxide components of the different profile materials were examined by measuring phosphate uptake, as well as that of certain dyes, and comparing the results with those obtained with authentic specimens of different iron oxide minerals, clay minerals, and laboratory preparations of hydroxides.

It is concluded that the significance and value of silica-sesquioxide ratios

may be considerable in the case of igneous rock-weathering products and soils, though doubtful in the case of sedimentary rock products containing secondary expanding clay minerals exhibiting ionic replacements in the lattice layers. The separate determination of free quartzose silica and of free gibbsitic alumina facilitates the interpretation of silica-alumina ratios in primary products of igneous rock weathering and further demonstrates the kaolinic nature of the aluminosiliceous component of the four materials comprising the red earth soil profile.

The classification of the parent materials of red soils is discussed in the light of these findings, and a provisional scheme and a nomenclature are submitted, based on determinations of their contents of gibbsite, kaolins, and iron oxide, and of less essential components, such as quartz, manganese oxide, and titania. The terms *laterite*, *lateritic*, and *kaolinic* are defined on this basis, and it is submitted that a more satisfactory description and definition of parent materials of red soils may be attained by these means than by field observations alone, and this should permit greater precision in identifying soil series.

APPENDIX

Dye adsorption tests for gibbsite, hydrous iron oxides, and clay minerals

The alizarin method for estimating gibbsitic alumina. The details of the modified method are as follows:

Two 1-gm. portions of air-dried material ground to pass a 100-mesh sieve, contained in silica weighing bottles, are ignited in a thermo-regulated electric muffle furnace at 750°C. for 15 minutes. After cooling, the ignited material is transferred to large boiling tubes, one containing 20 cc. of a 0.5 per cent solution of alizarin red S in boric alcohol, the other containing 20 cc. of boric alcohol alone. Both tubes are fitted with Hopkins-Cole reflux condensers and heated in a boiling-water bath for 10 minutes. The supernatant liquid in each tube is decanted into a 30-cc. silica Gooch crucible containing a pad of filter-paper pulp. In each case, the soil material in the tube is treated once with 20 cc. boric alcohol, boiled, and the whole transferred to the crucible and filtered by suction. Excess of dyestuff is next removed in one case by washing with several portions of boiling water until the filtrate is quite colorless. The duplicate ("blank") treatment is carried out in exactly the same manner, the material being given the same number of washings.

The stained portion is now "stripped" by treatment with boiling saturated aqueous sodium oxalate-oxalic acid solution at pH 3.8. The paper pad and stained material are returned to the boiling tube, adhering particles being washed off the crucible with oxalate solution. The volume is made up to about 30 cc., and the mixture is boiled, settled, and decanted into the Gooch crucible containing a fresh pad of paper pulp. The washing is repeated several times with small quantities of oxalate solution, and the volume is finally brought to a definite amount for the purpose of colorimetric comparison with a standard.

Suitable alizarin standards may be prepared by diluting 0.25 to 2.0 cc. of a stock 0.5 per cent aqueous solution of alizarin red S (the amount taken depending on the color of the "unknown") with an appropriate volume of "blank" oxalate extract of the unstained material; this corrects for color caused by iron and organic compounds soluble in the oxalate solution. One cubic centimeter of a 0.5 per cent dyestuff solution is taken as containing 100 dye units; thus, if both extract and standard are diluted to the same volume, and the standard contains 1.0 cc. of dyestuff solution, then, if the colors are exactly matched, the material has fixed 100 dye units per gram. Under such conditions, *ignited gibbsite* adsorbs

1,000 dye units per gram Al_2O_3 . Hence the percentage content of gibbsitic alumina in a sample under examination is obtained by multiplying its dye volume in units by 0.1.

The alizarin value of fresh *unignited* material is determined in exactly the same manner, the "blank" correction being applied in every case.

Preparation of Reagents. (a) *Alizarin solution.* Dissolve 5.0 gm. alizarin red S in 100 cc. water; complete the solution with 80 per cent alcohol saturated with boric acid (pH 3.2), and make up to 1 liter with boric alcohol. (b) *Oxalate solution.* Dissolve 42 gm. oxalic acid in 800 cc. water, add sufficient 40 per cent sodium hydroxide solution to give a reaction of pH 3.8, and make up to 1 liter with water. Filter off before use any sodium oxalate that may crystallize. (c) *Boric alcohol.* Dissolve 33 gm. boric acid in 1 liter of 80 per cent alcohol and filter off undissolved excess. Reaction, pH 3.2.

The diamine sky blue and the janus red tests. (a) *In borate solution:* Two 1-gm. portions of 100-mesh air-dried material are treated, one with 20 cc. dyestuff solution prepared by dissolving 0.2 gm. in a small volume of water and diluting to 100 cc. with 80 per cent alcohol saturated with boric acid, the other with 20 cc. boric-alcohol alone. The liquids are then decanted into Gooch crucibles containing disks of filter paper covered with glass dust, the subsequent treatments being the same as those in the alizarin test. "Stripping" is effected by means of alcoholic sodium hydroxide solution, prepared by mixing equal volumes of normal soda and 90 per cent alcohol. (Generally, the stripped material still retains some dye which cannot be removed except by drastic treatment.) Colorimetric comparison is conducted against a standard prepared by diluting an appropriate volume of the original 0.2 per cent dyestuff solution with "blank" extract, exactly as in the alizarin test. (b) *In phosphate solution:* The procedure is the same, except that a solution of the dyestuff in alcohol containing phosphate is employed instead of boric-alcohol. This is prepared by dissolving 0.2 gm. dyestuff in a small quantity of water and adding to it 10 cc. of an aqueous solution containing 2 gm. potassium dihydrogen phosphate (KH_2PO_4). The mixture is then diluted to 100 cc. with alcohol and water in such proportion that no precipitate forms. The reaction of the final reagent is about pH 5. A "blank" extract is also prepared for diluting the standard for colorimetric comparison.

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THE EFFECT OF FREE IRON OXIDE REMOVAL ON SOME PROPERTIES OF SOIL COLLOIDS¹

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In a previous contribution (9) some preliminary data were presented on the role of the free iron oxides in the phosphate-ion adsorption by soil colloids. It was pointed out that the removal of the free iron oxides from the colloids decreased the adsorption of phosphate ions. The phosphated residue, as a result of the decreased adsorption, possessed a smaller cation exchange capacity.

The purpose of the present investigation is to present further evidence to show that the treatment used for the removal of the free oxides of Fe, Al, and Si partially destroys the basoid properties of the colloids. The changes in the colloidal nature of the deferrated colloids have been approached essentially from the belief in the amphoteric behavior of the soil complexes (7). The data presented deal with ion adsorption, exchange capacity values, ultimate pH, and electrodialytic behavior of untreated and deferrated colloids.

For this study an attempt was made to obtain a series of colloids which would contain variable amounts of free iron oxides. Colloids were extracted from the following soil types by the method described previously (9):

Cecil clay subsoil: A new sample extracted from the 10-28-inch depth of a profile near Statesville, N. C.

Colts Neck loam: The A horizon of a virgin profile approximately 1½ miles southeast of Red Bank, N. J.

Penn silt loam: The middle of the B horizon of a virgin profile collected from a road cut about 2 miles south of Franklin Park on the road to Griggstown, N. J.

Sassafras loam: A new sample of the lower B horizon of a profile on the Wolpert Farm of the New Jersey Agricultural Experiment Station, New Brunswick.

EXPERIMENTAL METHODS

After extraction from the soils, the colloids were electrodialyzed free of exchangeable bases (8), and their chemical composition was established by the methods used for soil analysis. The composition is expressed in terms of samples dried to constant weight at 30°C.

The method of Drosdoff and Truog (4) was used to obtain the total free iron oxide content of the colloids. To obtain variations in the amounts of free iron

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oxide remaining in the colloid residue, the technic of the method was modified as follows: The series designated as treatment "A" in the following discussions were not digested with 2.5 per cent Na_2CO_3 solution but were rendered partially Na-saturated by washing twice with 50 cc. of N NaCl solution before being saturated with H_2S . The "B" series received the full treatment. After the removal of the oxides and free sulfur, the colloids of the two series were again partially Na-saturated by the previous treatment before being electro-dialyzed. This procedure was followed to aid in identifying the end point of electrodialysis as previously pointed out (8).

The anion adsorption experiments were generally performed at pH values that ranged from 2 to 6 and at concentration ranges of from 20–40 m.e. of anions per 10 gm. of colloid. The variations in pH ranges for the chloride system were obtained by mixing normal solutions of HCl and NH_4OH . With the phosphated series, varying pH values resulted when 0.5 N solutions of $(\text{NH}_4)_2\text{HPO}_4$ and H_3PO_4 were mixed. The quantity of chloride ion adsorbed was determined gravimetrically by precipitating and weighing the chloride as AgCl from an aliquot of the supernatant liquid of each system after adsorption. The usual volumetric procedure was used for determining the amount of phosphate ion adsorbed from an aliquot of the supernatant liquid after the removal of displaced silica by the usual method.

The cation exchange capacities of the original and deferrated electro-dialyzed colloids were determined by the barium acetate method (8). For the determination of the exchange capacity of the phosphated colloids, the samples, after ion adsorption, were transferred to a filter with 100 cc. of a normal NH_4Ac solution and then leached to 250 cc. with this solution to remove excess soluble phosphates prior to treatment of the samples with barium acetate solution.

The cation-saturated colloids were prepared by leaching 25 gm. of the H-colloids with 6 liters of normal neutral acetate solutions of the cations and then washing with 50 cc. of normal chloride solutions of the cations. The excess electrolyte was removed by washing with distilled water until the samples were free of chloride ions. The exchangeable cation content of the prepared colloids was determined by displacing the cations from a 2-gm. sample with a solution of normal neutral NH_4Ac and analyzing the filtrate for Ca, Ba, or Mg by the usual methods. For studying the release of cations by electrodialysis, a 10-gm. sample was placed in a Mattson cell and electro-dialyzed at a constant amperage of 0.4 for 24 hours in the case of the Ca- and Ba-colloids and for 48 hours in the case of Mg-colloids. Silica was removed from the catholyte prior to determining the cations by the usual methods. The residual cations not released by electrodialysis from the colloids were displaced by 500 cc. of normal neutral NH_4Ac and determined as described above.

The electro-dialyzed SiO_2 and R_2O_3 in the catholyte were determined by stabilizing the silica as SiO_2 and precipitating the R_2O_3 in the filtrate with NH_4OH . Iron was determined by reduction with stannous chloride and titration with 0.1 N KMnO_4 .

The neutralization curves of the untreated and deferrated colloids were obtained by the method of Anderson and Byers (2).

The pH values of all samples were obtained by the use of a glass electrode on colloid suspensions.

EFFECT OF THE DROSDOFF-TRUOG METHOD ON CERTAIN COLLOID PROPERTIES

The chemical composition of each of the colloid fractions extracted from the soils is presented in table 1. The silica-sesquioxide ratios of the colloids vary from 1.05 for the Cecil to 3.90 for the Sassafra. The composition of the Cecil and that of the Sassafra are identical with those reported previously for these colloids (9). The silica-sesquioxide ratios are somewhat higher because of the correction for the titanium which has been determined. The Colts Neck colloid isolated from the A horizon of the profile described previously is lower both in total Fe_2O_3 and Al_2O_3 than the colloid isolated from the B horizon of this profile. The free iron oxide content of the A horizon is, however, higher than that of the B.

The data presented in table 2 were obtained, as has been pointed out, by varying the technic of the Drosdoff-Truog method (4). This procedure was used rather than the newer modification (10), since the latter method resulted in a more intense degradation of the complex.

The differences between the free iron oxide contents of the colloids as determined by treatments A and B (table 2) may be explained in part by the following observations: During the digestion of the colloids with sodium carbonate solution, it was noted that mobilization of organic matter was more intense from the colloids that show differences in the free iron oxide content greater than 2 per cent by the two technics than from the others which did not show this variation. It is possible that humic acid gels protect the free iron oxides from reacting with the H_2S . If these gels are removed by digestion with alkali carbonates, however, the oxides do react. This preliminary digestion with the alkali carbonate also enhances the breakdown in acid of the silicate minerals. This fact is confirmed by the data in tables 2 and 3, which show a definite increase in silicate solubility by method B. The data in table 2 indicate only slight effects of treatment A on the cation exchange capacity of the colloids, whereas treatment B markedly affected the exchange power of the Colts Neck colloid. In the light of these findings, therefore, large batches of deferrated colloids were prepared by treatment A for later work. It should also be pointed out that if the organic matter had been removed from the colloid prior to determining the free iron oxide content, probably only slight effects would have been noted upon the exchange capacity. It is the author's belief, however, that soil colloids and their properties should be studied on samples as isolated from the soils, since the role of the organic matter fraction in colloids is equally as important as the role of the inorganic fraction.

The loss in weight of the various colloids as affected by the two treatments

TABLE 1
Chemical composition of soil colloids

COLLOID	$\frac{\text{SiO}_2}{\text{K}_2\text{O}}$	SiO_2	TiO_2	P_2O_5	Fe_2O_3	Al_2O_3	MnO	CaO	MgO	K_2O	C	WATER (105°C.)	IGNI- TION LOSS	CATION EXCHANGE CAPACITY (pH 7.0)	pH_u (H_2O)
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	m.e./gm.	
Cecil.....	1.05	34.48	0.68	0.05	14.34	45.76	0.19	0.04	0.58	0.42	0.48	2.23	4.00	0.107	5.30
Colts Neck.....	1.11	26.49	0.61	0.88	32.71	19.25	0.15	0.14	0.78	1.50	1.78	5.19	12.18	0.288	4.50
Penn.....	2.26	45.05	0.35	0.06	8.54	28.34	0.12	0.14	1.98	3.57	0.41	4.04	7.76	0.225	4.60
Sassafras.....	3.90	53.02	0.76	0.36	15.69	15.89	0.16	0.36	0.79	0.42	0.79	3.25	6.49	0.206	5.00

TABLE 2
Effect of free iron oxide removal upon cation exchange capacity and ultimate pH

COLLOID	TREATMENT A*			TREATMENT B†			CATION EXCHANGE CAPACITY			pH_u (H_2O)		pH_u (KCl)	
	Residue from 1-gm. sample	Per cent of total SiO_2 dissolved	Free Fe_2O_3	Residue from 1-gm. sample	Per cent of total SiO_2 dissolved	Free Fe_2O_3	Original colloid	Residue from treatment A	Residue from treatment B	Original colloid	Residue from treatment A	Original colloid	Residue from treatment B
	gm.	per cent		gm.	per cent		m.e./gm.	m.e./gm.	m.e./gm.				
Cecil.....	0.850	1.23	10.98	0.780	2.26	12.32	0.107	0.094	0.106	5.30	4.45	5.10	4.45
Colts Neck.....	0.667	3.39	19.58	0.484	9.47	28.27	0.288	0.302	0.205	4.50	4.30	4.20	4.20
Penn.....	0.896	1.24	3.58	0.827	4.75	4.96	0.225	0.237	0.202	4.60	4.45	4.25	4.30
Sassafras.....	0.837	1.76	6.13	0.772	4.09	7.58	0.206	0.204	0.208	5.00	4.35	4.90	4.30

* No preliminary digestion with 2.5 per cent Na_2CO_3 .

† Preliminary digestion with 2.5 per cent Na_2CO_3 .

is high, but it is surprising to note that the only colloid affected to any marked extent with respect to variations in exchange powers was the Colts Neck with treatment B. These results, in general, confirm previous data (9), namely, that only those colloids which possess acidoid fractions which mobilize at high pH values show reductions in exchange powers by the Drosdoff-Truog method. The greatest loss in weight due to treatment B, found with the Colts Neck colloid, represented nearly 50 per cent of the original weight based on oven-dried samples. Of this loss, approximately 35 per cent (table 3) represented solubility of the inorganic fraction. The residual loss of nearly 15 per cent is probably due to a loss of water of hydration from the destruction of the aluminum and iron silicates and solubility of organic matter. Losses from the Cecil, Penn, and Sassafras colloids were smaller than those from the Colts

TABLE 3

Composition of acid-soluble and electrodialyzable fractions from the Colts Neck and Penn colloids

Results in grams per 100 gm.

CONSTITUENT	ACID-SOLUBLE FRACTION (H ₂ S AND HCl)		ELECTRODIALYZABLE FRACTION FROM RESIDUE		ELECTRODIALYZABLE FRACTION FROM ORIGINAL COLLOID	
	Colts Neck	Penn	Colts Neck	Penn	Colts Neck	Penn
SiO ₂	2.032	1.251	0.080	0.051	0.038	0.010
Fe ₂ O ₃	28.270	4.960	0.029	0.010	0.012	0.006
Al ₂ O ₃	5.208	2.381	0.085	0.029	0.025	0.015
CaO	0.038	0.024	0.008	0.007	Trace	Trace
MgO	0.113	0.198	0.016	0.011	Trace	Trace
Total	35.661	8.814	0.218	0.108	0.075	0.031
SiO ₂ /Al ₂ O ₃	0.67	0.91	1.60	3.03	2.16	1.14

Neck and ranged from 18 to 23 per cent. The smaller losses from these colloids are due mainly to their lower content of free iron oxides.

It is generally admitted that the free oxides of Fe, Al, and Si possess little or no significant cation exchange powers (9); therefore, the removal of these constituents should not alter the exchange capacity of colloids. During the acid digestion of the black iron sulfides, however, fairly high amounts of Al, Si, Ca, and Mg are brought into solution (table 3) without affecting the exchange powers of certain colloids. Since the composition of the acid-soluble fraction for the colloids by treatment A is not available, only general statements can be made in regard to the solubility of the former constituents by this treatment. It is safe to assume that the effects of treatment A are less intense than those of treatment B (table 2), but still considerable quantities of silica and alumina are brought into solution. It would not be reasonable to assume that these constituents exist as free oxides in the colloids in such large quantities, and the general data do not indicate this. The only conclusion one can draw is

that a degradation of the complex results. In the light of these facts, what inferences can be drawn in regard to the acid solubility of colloidal material such that only slight effects are noted on the exchange capacity? It is possible that a differential solubility of aluminum silicates results and that these silicates are of low silica-sesquioxide ratio (0.5-1.0) and of low exchange capacity.

The pH values of the electrodialyzed colloids in water and in *N* KCl before and after the removal of the free iron oxides by both methods are presented in table 2. The ultimate pH values in water and in KCl solution of the untreated colloids bear a definite relation to the cation exchange capacity (7, 9). Because of exchange reactions, the values in KCl solutions are lower than those in water.

The electrodialyzed residues of treatment A with about the same exchange capacity as the untreated colloids have lower pH values in both water and KCl solutions than do the untreated colloids. The pH values are about the same for all the deferrated colloids, and no relation exists between the ultimate pH and the exchange capacity. The complete removal of the free oxides from the Colts Neck and Penn colloids has further reduced the ultimate pH by about 0.1 to 0.3 unit. The significance of the lowering of the ultimate pH of the colloids by the removal of the free oxides was at first questioned. This was due, in part, to the belief that the CS₂ used to extract the free sulfur may have been incompletely removed prior to and during electrodialysis. Since CS₂ is acid, the incomplete removal from the colloids might have lowered the ultimate pH. To test this point, the treatment for the removal of the free oxides was repeated, and simultaneously untreated colloids were subjected to similar washings with CS₂ and alcohol. The samples after washing, but in the moist condition, were placed on a steam bath, and the deferrated samples after this treatment were electrodialyzed as usual. Determinations of pH on the washed untreated samples and deferrated colloids yielded the same pH values as those recorded in table 2. From this behavior it was concluded that the effect of free oxide removal on reductions in the ultimate pH of the residues was correct.

To account for this behavior, one must conclude that the reduction in ultimate pH must be due, in part, to the H₂S, dilute acid treatment, and electrodialysis. The colloids, whether subjected to treatments A or B, lost a part of the nonexchangeable cations by acid solubility and hydrolysis. This is definitely indicated by the data in table 3 for treatment B. The former effects are less intense for treatment A than for treatment B. It should be noted from the data in table 3 that whereas the Colts Neck and Penn colloids lost 0.151 and 0.222 gm. per 100 of CaO plus MgO by solution and electrodialysis, the untreated colloids when rendered Na-saturated and electrodialyzed, yielded only traces of CaO and MgO. When hydrolyzed for 1 week in distilled water, however, the original colloids showed increases in ultimate pH as follows: Cecil, 0.3 unit; Colts Neck, 0.8 unit; Penn and Sassafra colloids, 0.4 unit, whereas the deferrated residues of treatment A showed only very slight elevations and those of treatment B showed none. Whether the loss of the part of

the nonexchangeable cations made soluble by the acid treatment and by electrodialysis can account for this variation in ultimate pH is uncertain. It is also possible that the removal of the gel envelopes by the free iron oxide treatment activates some of the acidoid fractions, and as a consequence an increased dissociation of H ions results (3).

The data presented in table 3 are in some respects similar to those reported by Truog and associates (10). The effects of the free iron oxide removal upon the release of aluminum and silica have been noted by these investigators. The effects of the treatment upon the release of a part of the nonexchangeable cations and the electrodialytic behavior of the deferrated colloids, however were not studied by Truog. The quantity of aluminum, silica, and calcium rendered soluble by the treatment is apparently independent of the composition of the colloid. This is indicated by the fact that the Colts Neck colloid with a silica-sesquioxide ratio of 1.11 lost more of these constituents as a result of the treatment than did the Penn colloid with a silica-sesquioxide ratio of 2.26. On the assumption that the silica and aluminum brought into solution represent the degradation of aluminosilicates of a definite composition, the silica-alumina ratios of the soluble fractions of the two colloids are fairly uniform, being 0.67 for the Colts Neck and 0.91 for the Penn colloid.

A comparison of the composition of the catholyte sediments from the original and deferrated residues brings out several interesting facts. The release of silica and the sesquioxides from the deferrated residues is greater than that from the untreated colloids. This may be due, in part, to the effect of the high pH on hydrolyzing silicate bonds in the clay lattices. If a hydrolysis of this nature occurred, however, a corresponding increase in exchange capacity would have resulted, and therefore the new complex would yield more silica and sesquioxides during electrodialysis (9). Since this increase was not noted, the alternative conclusion is that the removal of the oxide gel layers from around the crystalline nucleus enhances the degradation of the deferrated colloids. It is also surprising to note that the transport of iron during electrodialysis is greater with the deferrated residues of the Colts Neck and Penn colloids than with the original colloids even though 6 to 28 per cent of the total iron has been removed by the treatment. An explanation for this is that the free iron oxides in the original colloids are not mobilized during electrodialysis (9). Not all colloids, however, behave as do the Colts Neck and Penn upon partial deferration. In table 4 are presented data with reference to the release of silica, iron, and aluminum during the electrodialysis of Mg-saturated colloids. Although the release of silica and of total R_2O_3 is always greater with the deferrated than with the original colloids, the composition of the R_2O_3 precipitate varies. In some cases, as with the Colts Neck and Penn colloids, the release of iron from the deferrated colloids is greater than that from the original colloids, whereas with the Cecil and Sassafra, the release is greater from the untreated colloids. With all the colloids, the release

TABLE 4

Release of SiO_2 and R_2O_3 from original and from deferrated Mg-saturated colloids during electro dialysis

Results in milligrams per 100 gm.

COLLOID	TREATMENT	SiO_2	R_2O_3	Fe_2O_3	Al_2O_3	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$ COLLOID	CATHOLYTE SEDIMENT $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$
Cecil	None	30.0	72.0	22.0	50.0	1.26*	1.02
	Deferrated	72.0	140.0	8.0	132.0	0.93
Colts Neck	None	48.0	128.0	55.2	72.4	2.34*	1.11
	Deferrated	204.0	360.0	103.4	256.6	1.35
Penn	None	80.0	96.0	22.0	74.0	2.69*	1.41
	Deferrated	92.0	128.0	32.0	96.0	1.62
Sassafras	None	66.0	128.0	27.0	101.0	5.70*	1.00
	Deferrated	72.0	180.0	22.0	158.0	0.77

* Of untreated colloids.

TABLE 5

Adsorption of chloride ion by untreated and by deferrated colloids

COLLOID	Cl^- ADDED AS $\text{HCl} + \text{NH}_4\text{OH}$	FREE IRON OXIDE CONTENT		pH OF SUPERNATANT LIQUID		Cl^- ADSORBED	
		Original	Deferrated A	Original	Deferrated A	Original	Deferrated A
	<i>m.e./10 gm.</i>	<i>per cent</i>	<i>per cent</i>			<i>m.e./10 gm.</i>	<i>m.e./10 gm.</i>
Cecil	20.00	3.70	3.70	0.320	0.000
	20.00	12.32	1.44	2.00	2.10	0.480	0.000
	20.00	1.80	1.80	0.520	0.020
Colts Neck	20.00	3.90	3.50	0.040	0.000
	20.00	25.27	8.69	2.20	2.00	0.070	0.003
	20.00	1.80	1.80	0.320	0.010
Penn	20.00	3.30	3.30	0.270	0.000
	20.00	4.96	0.58	1.90	1.90	0.380	0.000
	20.00	1.60	1.60	0.480	0.070
Sassafras	20.00	4.00	4.00	0.070	0.000
	20.00	7.58	1.45	2.25	2.10	0.380	0.000
	20.00	1.75	1.75	0.500	0.027

of aluminum is always greater from the deferrated residues. The silica-aluminum ratio of the catholyte sediment is always less than that of the original colloid. This behavior has been discussed elsewhere (9).

CHANGES IN ANION ADSORPTIVE ABILITY OF SOIL COLLOIDS RESULTING FROM
REMOVAL OF FREE IRON OXIDES

The essential changes in the properties of soil colloids that might be expected as a result of the removal of the free iron oxides are reductions in the ability of the clays to adsorb anions, variations in the mechanism of the adsorption, and possible changes in neutralization curves at high pH values. The data presented here deal with the adsorption of both chloride and phosphate ions by the original and by the deferrated colloids. The nature and the mechanisms involved in the adsorption of phosphate ions by the completely deferrated residues are also discussed.

The data presented in table 5 are concerned with the adsorption of chlorides by the various colloids. If the adsorption of this ion is based on the order of activity manifested by the ultimate pH of the colloids, the order should be Cecil, Sassafras, Penn, and Colts Neck. At the lowest pH for the various systems of the original colloids, this order is followed, for the Cecil adsorbs 0.52 m.e., the Sassafras 0.50 m.e., the Penn 0.48 m.e., and the Colts Neck 0.38 m.e. per 10 gm. It is also to be noted that the adsorption increases with decreasing pH (7, 9). The partial removal of the free iron oxides from the colloids has decreased the adsorption of the chloride ion. This significant fact points toward a definite role of the free iron oxides in the adsorption of chloride ions. Since the hydrated iron oxides are responsible for phosphate adsorption, as pointed out by Ford (5), the possibility that chloride ion adsorption may be due to these oxides is suggested here.

The adsorption of phosphate ions by the differently treated colloids is presented in table 6. Certain general conclusions with respect to the adsorption of these anions by the colloids may be deduced from the data. These general facts are that phosphate ion adsorption increases both with increasing anion concentration and with decreasing pH. These points were discussed previously (9). The dependence of the magnitude of adsorption by the colloids upon the silica-sesquioxide ratio, free iron oxide content, and displaced silicates is an outstanding point in table 5. In addition, several significant new facts are apparent.

The phosphate ion adsorption decreases with the completeness of removal of the free iron oxides from the soil colloids, but even with the completely deferrated residue, the adsorption, unlike that of chloride, is rather great. Since it has been pointed out previously (9) that the retention of phosphate ions by the hydrated iron oxides occurring in the colloids is responsible, in part, for the increases in cation exchange capacity, the partial removal of these minerals markedly reduces the cation exchange capacity of the phosphated residues. With the Colts Neck and Sassafras colloids of the treatment B series, phosphate ion adsorption was not associated with increases in cation exchange capacity even though the ion adsorption of the residues amounted to 25 to 50 per cent of the total adsorbed by the original colloids. With the Cecil

TABLE 6
Adsorption of phosphate ions by untreated and by deferrated colloids

COLLOID	FREE Fe ₂ O ₃ CONTENT				PO ₄ = ADDED AS H ₂ PO ₄ + NH ₄ OH	pH OF SUPERNATANT LIQUID			PO ₄ = ADSORBED			CATION EXCHANGE CAPACITY			SILICA IN SUPERNATANT LIQUID		
	Treat- ment A		Treat- ment B			Original	Treat- ment A	Treat- ment B	Original	Treat- ment A	Treat- ment B	Original	Treat- ment A	Treat- ment B	Original	Treat- ment A	Treat- ment B
	per cent	per cent	per cent	per cent													
Cecil	12.32	1.44	0.00		m.e./ 10 gm.	5.30*	4.30*	m.e./ 10 gm.	1.07	0.94	1.06	m.e./ 10 gm.
					0.00	5.60	4.50	4.62	1.29	1.66	1.45	3.73	3.72
					25.00	3.20	3.40	4.71	2.17	0.86	2.02	1.62	1.25	4.24	5.76	5.68
					30.00	3.55	2.85	2.85	7.41	4.80	2.54	2.30	1.71	1.48	5.76	5.60	8.10
Colts Neck	28.27	8.69	0.00		40.00	3.00										
					0.00	4.50*	4.30*	2.88	3.02	2.05
					25.00	6.02	5.90	5.48	3.09	4.96	3.21	6.73	4.80
					30.00	4.38	3.68	3.69	7.03	3.67	3.25	5.24	3.55	2.00	9.40	5.60	5.60
Penn					40.00	3.20	2.92	2.70	9.26	5.45	5.06	5.67	3.78	2.05	9.60	7.36	7.12
					0.00	4.60*	4.45*	2.25	2.37	2.02
	4.96	0.58	0.00		25.00	4.80	5.00	5.19	2.46	3.24	2.89	5.12	4.52
					30.00	3.62	3.58	3.28	5.37	3.55	2.30	3.75	3.10	2.48	7.36	6.29	8.00
Sassafras					40.00	3.05	2.85	2.71	6.23	4.80	2.69	3.92	3.36	2.56	8.56	7.68	8.00
					0.00	5.00*	4.35*	2.06	2.04	2.08
	7.58	1.45	0.00		25.00	5.73	4.70	3.33	2.61	2.84	2.52	6.00	7.26
					30.00	3.88	3.35	3.38	5.49	2.63	2.03	3.38	2.72	2.07	6.96	7.68	9.12
				40.00	3.00	2.80	2.70	8.84	4.28	2.30	3.87	2.86	2.06	7.04	8.16	8.82	

* 1:10 suspensions.

and Penn colloids only slight increases were found in cation exchange capacity of the treatment B residues after phosphate ion adsorption.

Two reasons might be advanced for the adsorption by the colloid residues of the B series without appreciable increases in cation exchange capacity. The adsorbed phosphate ions might be so weakly retained by the residues that the preliminary washing with N NH_4Ac and BaAc_2 completely displaced the adsorbed ions. To clarify this point, samples of the original and of the residues from the B treatments of the Colts Neck and Penn colloids were allowed to adsorb phosphate ions from a mixture of phosphoric acid and ammonium phosphate solutions. The cation exchange capacities of the treated colloids were determined by the procedure outlined in the experimental methods. The total phosphate content of the original and phosphated colloids was

TABLE 7

Adsorption of phosphate ions by untreated and by deferrated Colts Neck and Penn colloids in relation to changes in exchange capacity

COLLOID	PO_4^{3-} ADDED AS $\text{H}_2\text{PO}_4 +$ $(\text{NH}_4)_2$ HPO_4	pH OF SUPERNATANT LIQUID	PO_4^{3-} RETAINED	CATION EXCHANGE CAPACITY	INCREASE IN CATION EXCHANGE CAPACITY	SILICA IN SUPERNATANT LIQUID
	<i>m.e./12 gm.</i>		<i>m.e./12 gm.</i>	<i>m.e./12 gm.</i>	<i>m.e./12 gm.</i>	<i>m.e./12 gm.</i>
Colts Neck—"O"	0.0	3.43
	25.0	5.65	4.75	5.82	2.39	1.19
Colts Neck—"B"	0.0	2.46
	25.0	5.65	1.62	2.50	0.04	2.43
Penn—"O"	0.0	2.75
	25.0	4.55	2.76	4.41	1.66	1.39
Penn—"B"	0.0	2.42
	25.0	4.45	1.16	2.68	0.26	2.00

determined on the samples used for exchange capacity determinations after the displacement of the adsorbed Ba by 0.05 N HCl . These data, presented in table 7, definitely indicate that the strength of the retention of the adsorbed phosphate ions by the deferrated residues and the original colloids is great enough to prevent displacement by salt solutions. The data in table 7 also confirm the facts found from the previous table.

Since it has previously been noted (9) that the adsorption of phosphate ions by electrodialyzed soil colloids may be due in part to the displacement of silicate ions from the lattice by phosphate ions, it is possible that a displacement of this nature is not associated with increases in cation exchange capacity. With reference to the displacement, it is interesting to note from both tables 6 and 7 that, in general, the quantities of silica in the supernatant liquid from the deferrated residues are larger than those from the original colloids at

equivalent pH values and phosphate-ion concentrations. This mechanism of phosphate ion retention by soil colloids is being studied further.

The neutralization curves of the original and deferrated Colts Neck and the Penn colloids are presented graphically in figure 1. The usual procedure of plotting pH against cubic centimeters of alkali was not followed, since the purpose of this study was not to compare the neutralization curves of different colloids but to compare the curves of the original and deferrated residues of the same colloid. The curves were obtained, therefore, by plotting the alkali

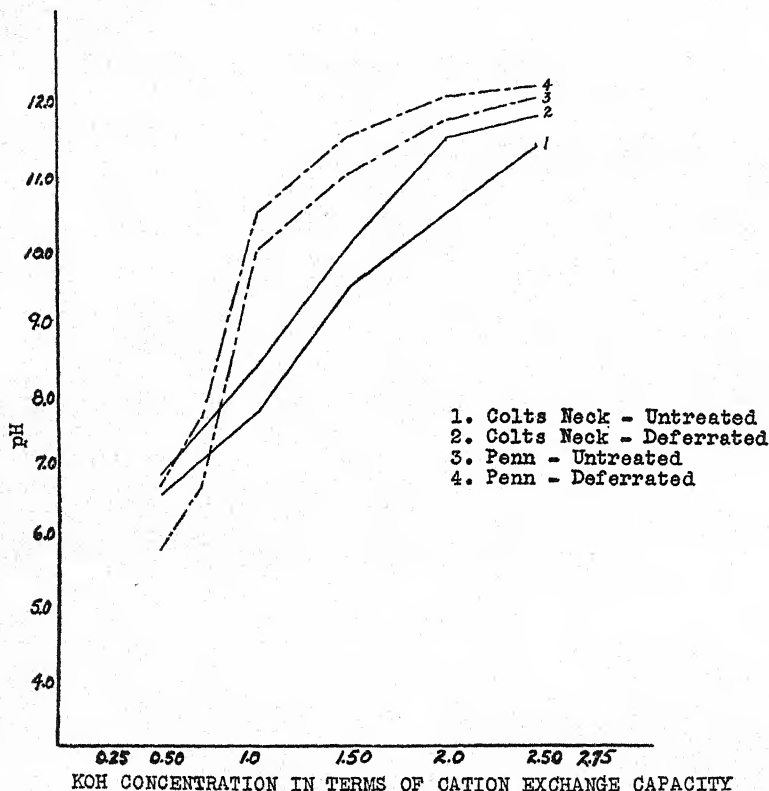


FIG. 1. NEUTRALIZATION CURVES OF UNTREATED AND DEFERRATED COLTS NECK AND PENN COLLOIDS

expressed in terms of the cation exchange capacity at pH 7.0 against the pH of the suspension, at equilibrium, of the H-colloids and the alkali. From figure 1, the outstanding feature of the curve for either colloid is that the neutralization curve of the deferrated colloid, though similar to the curve for the original colloid, is obtained at higher pH values. This behavior points to a definite reduction in the neutralization capacity of the deferrated residues for alkali. As previously pointed out, both the free iron oxides and the aluminosilicates are removed from the colloids by the iron oxide removal treat-

ment, and since both of these constituents can combine with alkali, the reduction in neutralization capacity can account for the variations between the curves. The curves for the Cecil and Sassafras colloids are essentially similar to those obtained for the Colts Neck and Penn, and are not, therefore, presented.

EFFECT OF FREE IRON REMOVAL ON RETENTION AND RELEASE
OF Ca, Ba, AND Mg BY ELECTRODIALYSIS

The changes in the properties of soil colloids produced as the result of the partial removal of the basoid fraction have been emphasized. It is the purpose of the following experiment to note whether or not alterations have resulted in the nature of the acidoid fraction of the colloids. Since the nature of the acidoid fraction influences to some extent the retention of specific cations by

TABLE 8
Cation content and pH values of H-, Ca-, Mg-, and Ba-colloids

COLLOID	CATION CONTENT			pH VALUES (1:10 H ₂ O)			
	Ca	Mg	Ba	H	Ca	Mg	Ba
	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>				
<i>Untreated Colloids</i>							
Cecil.....	11.05	10.40	9.40	5.30	7.20	6.00	6.40
Colts Neck.....	30.79	31.90	28.80	4.50	6.50	5.40	6.60
Penn.....	23.21	23.00	22.50	4.60	6.30	5.70	6.50
Sassafras.....	20.21	16.30	16.50	5.00	6.80	5.70	6.40
<i>Deferrated Colloids</i>							
Cecil.....	11.12	10.00	10.08	4.30	6.80	4.90	6.25
Colts Neck.....	31.29	32.90	28.80	4.30	6.90	4.50	6.50
Penn.....	23.21	21.50	19.80	4.45	6.90	5.30	6.35
Sassafras.....	21.76	16.50	22.50	4.35	6.20	4.80	6.30

colloids, it was believed that a study of the release of Ca, Mg, and Ba from cation-saturated colloids during electrodialysis would yield data concerned with changes in the acidoid fractions. With this object in view, the data in tables 8 and 9 are presented. The data in these tables differ in one main respect from the data in previous tables. For the purpose of comparing the release of cations during electrodialysis, equal quantities, with respect to the content of each specific cation, of the original and deferrated colloids were used rather than the weights of the residues of varying exchange capacity. The corrections for this variation were generally slight, with the exception of the Colts Neck colloid. In table 8, therefore, it should be noted that the exchangeable cation contents of the original and the deferrated colloids are approximately the same. Variations do exist in the degree of saturation of the colloids with specifications but it is believed that this is due, in part, to the technic

employed in preparing the cation-saturated colloids. The pH values must also be examined and compared on basis of the cation content and not on the basis of equal saturation.

It has been pointed out (6) that, in general, for cations fixed by colloids, the stability of the retained cation depends upon the silica-sesquioxide ratio. Less Mg is released during electrodialysis from colloids of high silica-sesquioxide ratio than from colloids of a low ratio (6). This is believed to be due to the greater stabilization of exchangeable Mg by colloids of a high silica content. Generally the pH values of Mg-saturated colloids are lower than the pH values of Ca-saturated colloids (1, 6) and this behavior is also advanced as a further proof of the stabilization of exchangeable Mg by soil colloids. The pH values of the colloids presented in table 8 afford excellent data for an examination of the foregoing theory.

Since the original and deferrated Sassafras colloids are only partially saturated with Mg and Ba, the data on these clays will be omitted from the following discussion.

The pH values of the cation-saturated colloids as presented in table 8 are of particular interest. The pH values of the Mg-saturated colloids are lower than those of the Ca- or Ba-saturated colloids by 0.4 to 1.2 pH unit with the original and from 1 to 2.4 pH units with the deferrated residues. This behavior is in line with the previously cited facts (1, 6). Only slight differences exist between the pH values of the Mg-saturated colloids in relation to the silica-sesquioxide ratio. This may, of course, be due to the fact that other acidoids (6) interfere in the evaluating of the correlation. Only slight differences are to be noted from the data in table 8 with respect to the pH values of the original Ca- and Ba-saturated colloids with the exception, however, of the pH of the original Cecil colloid. This colloid has a pH value about 0.8 higher for the Ca- than the Ba-saturated sample. The difference in pH between the deferrated residues and the original colloids is not very significant for the Ba-saturated samples. For the Ca-saturated samples, however, the difference is in favor of the residues with the Penn and Colts Neck and in favor of the original colloids with the Cecil and Sassafras. No relation exists between the silica-sesquioxide of the colloids and the pH values of the Ca- or Ba-colloids.

The release of cations by electrodialysis from the various colloids is presented in table 9, as well as the residual exchangeable cation content of the electro-dialyzed colloids. The total recovery of cations by electrodialysis and salt displacement is also given in table 9. From the data concerned with the release of exchangeable Ca and Ba, it will be noted that only slight differences exist between the original and the deferrated colloids. The differences range from 0.6 per cent with the Cecil to 8.4 with the Penn colloid. With the Mg-colloids only slight differences exist between the original Penn and Sassafras and the deferrated residues of these two colloids, but significant variations do exist with the Colts Neck and Cecil colloids. The fact that less Mg is released from these two deferrated colloids by electrodialysis indicates a definite change

TABLE 9
Release of cations by electro dialysis from untreated and deferred colloids
 Time of electro dialysis, 24 hours for Ca and Ba; 48 hours for Mg

COLLOID	CATIONS RELEASED BY ELECTRODIALYSIS			PER CENT OF TOTAL CATIONS RELEASED BY ELECTRODIALYSIS			CATIONS DISPLACED BY <i>N</i> <i>NH</i> ₄ Cl AFTER ELEC- TRODIALYSIS			PER CENT OF TOTAL CATIONS DISPLACED BY <i>N</i> <i>NH</i> ₄ Cl AFTER ELEC- TRODIALYSIS			RECOVERY OF CATIONS		
	Ca	Ba	Mg	Ca	Ba	Mg	Ca	Ba	Mg	Ca	Ba	Mg	Ca	Ba	Mg
	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>				<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>				<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
<i>Untreated Colloids</i>															
Cecil.....	10.06	8.60	8.00	91.0	95.5	76.9	0.99	0.59	0.92	9.0	2.2	8.8	100	97.7	85.7
Colts Neck.....	27.70	27.46	18.00	89.9	95.3	56.4	2.99	0.59	1.70	10.1	2.0	5.3	100	97.7	61.7
Penn.....	22.22	20.37	21.60	95.7	90.5	93.9	0.99	1.00	1.40	4.3	4.4	6.1	100	94.9	100
Sassafras.....	19.22	15.60	13.80	95.1	94.5	84.6	0.99	0.69	2.50	4.9	4.3	15.4	100	98.7	100
<i>Deferred Colloids</i>															
Cecil.....	10.06	9.58	6.22	90.4	95.8	62.2	1.06	0.45	1.64	9.6	3.8	16.4	100	99.3	78.6
Colts Neck.....	28.50	25.94	14.96	91.1	90.0	45.4	2.79	0.45	1.22	8.9	1.6	3.8	100	91.6	49.2
Penn.....	22.31	19.20	19.06	96.1	98.9	88.6	0.89	0.40	1.40	3.9	1.1	6.5	100	100	95.1
Sassafras.....	20.86	21.60	14.74	95.8	96.0	89.3	0.90	0.59	1.00	4.2	3.6	6.0	100	99.6	95.3

in the nature of acidoid linkages. The removal of phosphorus and organic matter during the treatment of the colloids probably accounts for this variation, since the magnesium silicates are less soluble than compounds of magnesium with phosphoric or humic acids. The rate of release of Mg during electrodialysis is also less than that of either Ca or Mg, as the data in table 9 indicate. Complete recovery of Ca and Ba within experimental error from the colloids by electrodialysis and salt displacement indicates no fixation of these cations by the colloids. For Mg, however, definite indications of fixation were obtained with the Cecil and Colts Neck colloids, whereas a complete recovery was noted with the Penn and Sassafras colloids. Apparently, other factors besides the silica-sesquioxide ratio influence the release and fixation of Mg.

SUMMARY

A study was made of the effects of free iron oxide removal from soil colloids upon certain properties of the colloids.

It was observed that the deferrated colloids lost more silica and sesquioxides during electrodialysis than did the untreated colloids. The composition of the sesquioxides varied, but the amount of aluminum electrodialyzed from the deferrated residues was always greater.

The removal of the free oxides lowered the ultimate pH of the colloids without materially affecting the cation exchange capacity at pH 7.0.

The removal of the free oxides decreased the adsorption of chloride and phosphate ions. Indications that soil colloids may adsorb phosphate ions without altering the cation exchange capacity were obtained with completely deferrated Colts Neck and Sassafras colloids.

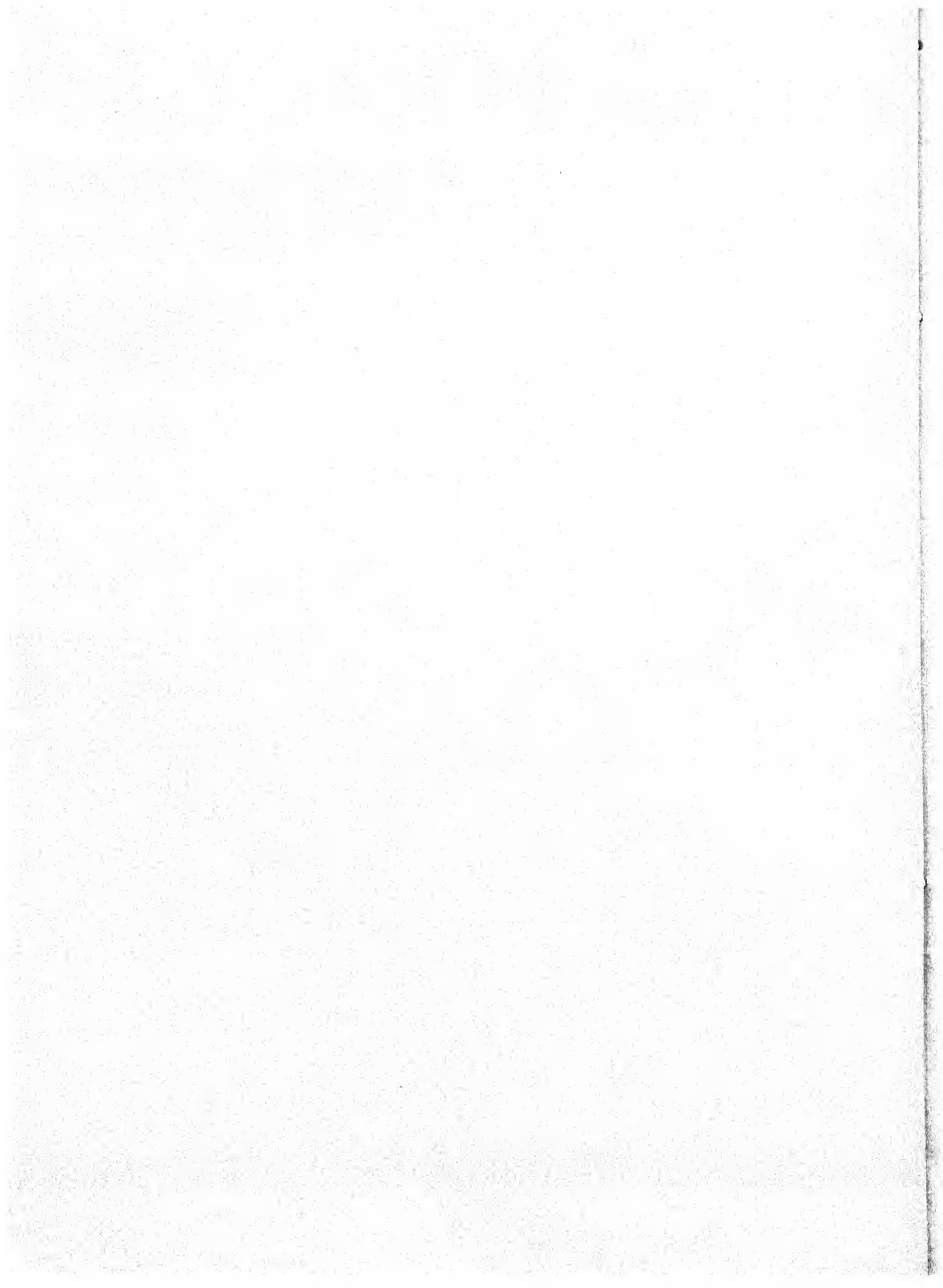
The neutralization curves of the deferrated colloids were similar to the curves for the original colloids, but the residues possessed a lower buffer capacity.

The effect of free oxide removal upon the nature of the acidoid fraction was also studied. Only slight changes were observed, and these were ascribed to the removal of certain acidoids. In general, the release by electrodialysis of Ca and Ba from original and deferrated colloids was the same. Magnesium, however, differed from the former two cations in that less was released per unit time from the colloids by electrodialysis.

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RELIABILITY OF THE PROPOSED SUCTION METHOD OF DETERMINING THE MOISTURE EQUIVALENT OF SOILS¹

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The moisture equivalent is now rather generally recognized in this country as a fairly reliable measure of the texture of the soil (6) and "the moisture equivalent centrifuge is now a recognized piece of apparatus in well equipped soil physics laboratories" (5). In this laboratory the centrifuge has been in constant use for 25 years. As the apparatus is expensive and requires an electric current for its operation, there is a place for some method that will give the same values while requiring only simple equipment. To meet this need Bouyoucos (1, 2) has proposed a suction method requiring only such apparatus as is to be found in any chemical laboratory. He considers it rapid, accurate, and reliable, in addition to being simple and convenient. In his first paper describing the method (1) he gave no comparison of values obtained by the two methods, but in his second he reports such a comparison for 25 soils, the determinations by his method being made in his laboratory and the centrifuge being used with 13 of the soils at both Cornell University and the U. S. Department of Agriculture at Washington, 10 at only the former, and 2 at only the latter. Apparently, no determinations with the centrifuge were made in his own laboratory on the soils dealt with in his papers.

Shortly before the appearance of Bouyoucos' second paper a comparison of the two methods, using over one hundred soils, had been completed at this laboratory. The modifications of the suction method proposed in the second paper made a study of these desirable before the comparison was published, a study that circumstances have prevented until the present.

MOISTURE EQUIVALENT DEFINED

The term *moisture equivalent* was introduced by Briggs and McLane in 1907 (3, p. 5) to designate "the percentage of water retained by a soil when the moisture content is reduced by means of a constant centrifugal force until it is brought to a state of capillary equilibrium with the applied force." At that time, using a centrifugal force 3,000 times gravity, they reported the moisture equivalents of 100 soils of known mechanical composition. Three years later (4) they adopted "as a standard basis of comparison a centrifugal force equal

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to 1,000 times the force of gravity, one centimeter as the thickness of the soil layer when packed in the cup and 40 minutes as the time of operation of the machine at the designated speed, 2440 r.p.m." They adopted 20°C. as the standard temperature but found the temperature effects so small that they can usually be disregarded.

Russel and Burr (5), as the result of a detailed study of "the effect of speed, period of centrifuging and depth of soil layer in the cup on the moisture equivalent . . . in an attempt to arrive at either a less empirical definition of the moisture equivalent or a better appreciation of the necessity of strict adherence to the present adopted procedure," concluded that "the moisture equivalent is best defined as Briggs and McLane have defined it, that is, centrifugal force 1000 g; depth of soil, 10 mm.; period, 40 minutes," remarking that "it is indeed fortunate that so near the desirable requirements were decided upon."

DESCRIPTION OF THE SUCTION METHOD

The method described in Bouyoucos' first paper consists of connecting a small Buechner funnel with a suction flask, placing on this a filter paper, filling the funnel three-fourths full of air-dry soil, thoroughly soaking this with water, connecting the flask to the suction pipe on a faucet and then allowing the suction force from the running water to operate on the soil for about 12 minutes, the funnel being covered with a moist thick cloth, in order to prevent evaporation during the suction process. The funnel is then removed from the suction flask, the soil scraped into a weighing receptacle and its moisture content determined in the usual way. In his second paper he specifies a funnel 50 mm. in diameter and 25 mm. high, first passing the air-dry soil through a 2-mm. sieve, filling the funnel full and then compacting the soil by gently tapping the lower end of the funnel against the table. Also, instead of wetting the soil in the funnel by adding water to the surface, the filled funnel is placed in a beaker into which water is poured until it almost reaches the level of the top of the funnel and left for about 24 hours. The attempt is made to maintain in the funnel the same depth of wet soil, and not the same weight of dry soil, by levelling off the soil even with the top of the funnel after the soil has been suctioned for a minute and has become settled and compacted. The weight of the dry soil used in his determinations varied from about 40 to 85 gm., depending upon the class of soil. Suction is continued for 15 minutes after all the excess water on the top of the soil has disappeared, and during suction the soil is covered with a tumbler containing a moist cloth. The values obtained with a water jet pump giving a vacuum pressure of only about 15 mm. were similar to those found with a high vacuum pump, giving a vacuum of 4 mm.

EXPERIMENTAL

In our comparison, 113 Minnesota soils selected from samples on hand at our laboratory so as to cover a wide range in moisture equivalent, were used.

They represent 15 different soil series in addition to muck and leafmold. About a third are surface samples, the others from various depths down to the sixth foot. The nitrogen content ranges from 0.001 to 2.03 per cent, and the pH value, from 4.7 to 8.1. The data on 23 representative soils are reported in table 3. The numbers in the first column indicate the order in moisture equivalent value, No. 1 being the soil with the lowest, 1.5, and No. 113 that with the highest, 90.6.

TABLE 1

Effect of depth of soil in Buechner funnel upon the amount of water retained after suction

REFERENCE NUMBER	WATER RETAINED* AFTER SUCTION			DIFFERENCE BETWEEN DUPLICATE DETERMINATIONS WITH SOIL DEPTH OF	
	With soil depth of		Excess with deeper layer	20 mm.	25 mm.
	20 mm.	25 mm.		20 mm.	25 mm.
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	4.2	4.5	0.3	0.7	0.9
2	4.3	4.7	0.4	0.7	0.6
3	3.6	3.9	0.3	0.1	0.1
4	4.0	5.1	1.1	0.2	0.2
5	4.4	6.2	1.8	0.0	0.9
6	4.2	4.6	0.4	0.3	0.4
7	4.8	9.2	4.4	0.6	0.5
8	4.6	7.6	3.0	0.2	1.1
9	6.7	7.1	0.4	1.7	2.2
35	18.6	16.8	-1.8	1.2	1.1
36	18.9	24.1	5.2	0.8	0.4
40	20.3	19.5	-0.8	0.3	1.9
44	24.8	27.8	3.0	0.0	0.9
61	32.5	31.0	-1.5	0.8	1.4
65	33.1	30.1	-3.0	1.7	0.6
71	36.3	39.9	3.6	1.9	1.3
80	36.6	39.7	3.1	3.6	2.2
84	39.7	40.9	1.2	1.7	0.1
87	42.2	43.6	1.4	5.2	0.2
95	48.5	48.6	0.1	0.3	1.2
Average. . . .	19.6	20.7	1.1	1.1	0.9

* Average of duplicate determinations.

Though the Buechner funnel used was of the size specified in Bouyoucos' second paper, the depth of the air-dry soil placed in it was that specified in his first paper, approximately 20 mm. ("funnel three-fourths full"). The soil was moistened, as described in the first paper, by adding water to the surface at intervals of 10 to 15 minutes after it had begun to drain from the funnel and not by allowing the funnel to stand in a beaker of water. A few of the soils very rich in organic matter absorbed water so slowly that with them the addition was continued at intervals for an hour or more. The determinations

by the centrifuge as well as by suction were made in duplicate. With the latter where the values were widely discordant a third or even a fourth determination was made and the average of the closest two reported in the table.

In order to decide whether the proposed increase in depth of the air-dry soil in the funnel or the change in method of wetting it would lessen or increase the amount of water retained after suction, we have now repeated the determinations on 20 of the soils, using the 9 coarsest in texture and 11 of finer texture

TABLE 2

Effect of method of wetting the soil in Buechner funnel upon amount of water retained after suction

REFERENCE NUMBER	WATER RETAINED* AFTER SUCTION			DIFFERENCE BETWEEN DUPLICATE DETERMINATIONS WHEN SOIL WAS WETTED FROM	
	Soil wetted from		Excess with latter	Above for 15 min.	Below for 7 hours
	Above for 15 min.	Below for 7 hours			
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	4.5	4.1	-0.4	0.9	0.0
2	4.7	5.8	1.1	0.6	1.0
3	3.9	4.3	0.4	0.1	3.1
4	5.1	3.8	-1.3	0.2	0.3
5	6.2	6.4	0.2	0.9	0.8
6	4.6	6.6	2.0	0.4	2.4
7	9.2	8.3	-0.9	0.5	0.4
8	7.6	8.1	0.5	1.1	0.9
9	7.1	9.0	1.9	2.2	4.3
35	16.8	17.6	0.8	1.1	2.2
36	24.1	24.8	0.7	0.4	2.0
40	19.5	18.6	-0.9	1.9	0.4
44	27.8	25.8	-2.0	0.9	3.1
61	31.0	35.8	4.8	1.4	5.2
65	30.1	32.3	2.2	0.6	4.9
71	39.9	44.1	4.2	1.3	6.1
80	39.7	45.2	5.5	2.2	3.0
84	40.9	41.7	0.8	0.1	3.1
87	43.6	44.8	1.2	0.2	1.7
95	48.6	47.8	-0.8	1.2	1.0
Average	20.8	21.7	0.9	1.0	2.3

* Average of duplicate determinations.

which had shown the greatest difference between moisture equivalent and suction value. Neither the values obtained with the thicker layer of soil (table 1) nor those from the prolonged wetting (table 2) depart definitely from those obtained earlier. We conclude, therefore, that the suction values of the remaining 93 soils would not have been significantly different had they been determined with a greater depth in the funnel and kept in contact with water over night.

The term *suction value* is used in this paper merely to differentiate in the discussion the amount of water retained by a soil when subjected to the treatment described in Bouyoucos' second paper from the value obtained with the centrifuge and not with the idea of introducing it into soils literature. If the values obtained by the suction method are the same as those from the centrifugal method they also may properly be referred to as *moisture equivalents*,

TABLE 3
"Suction values" of representative soils compared with their moisture equivalents

REFERENCE NUMBER	COUNTY	SOIL SERIES	DEPTH OF SECTION	N	pH	MOISTURE EQUIVALENT	SUCTION VALUE	EXCESS OF MOISTURE BY SUCTION	RATIO OF SUCTION VALUE TO MOISTURE EQUIVALENT	DIFFERENCE BETWEEN DUPLICATE DETERMINATIONS	
										Moisture equivalent	Suction value
			inches	per cent		per cent	per cent			per cent	per cent
1	Aitkin	Grayling	61-72	0.001	5.7	1.5	4.2	2.7	2.80	0.0	0.7
7	Aitkin	Grayling	13-24	0.010	5.5	2.9	4.8	1.9	1.66	0.1	0.6
8	Aitkin	Rabey	25-36	0.014	5.6	3.0	4.6	1.6	1.53	0.2	0.2
11	Aitkin	Munger	61-72	0.001	6.4	4.8	6.1	1.3	1.27	0.1	1.0
15	Aitkin	Cloquet	13-24	0.017	5.1	6.0	7.0	1.0	1.17	0.6	0.8
18	Aitkin	Swan	25-36	0.008	7.5	7.2	9.2	2.0	1.28	0.1	0.5
22	Aitkin	Hill City	1-6	0.061	5.0	9.0	9.8	0.8	1.09	0.3	1.9
31	Aitkin	Kingsley	3-19	0.049	5.0	12.8	14.6	1.8	1.14	0.1	1.4
37	Lac qui Parle	Moody	1-6	0.198	6.2	16.0	21.0	5.0	1.31	0.4	1.9
45	Jackson	Bremer	13-24	0.090	6.7	21.2	22.5	1.3	1.06	0.6	5.0
50	Houston	Tama	13-24	0.056	5.2	23.1	28.5	5.4	1.23	0.2	0.3
52	Rice	Carrington	1-6	0.263	5.5	24.0	27.0	3.0	1.12	1.2	0.1
54	Fillmore	Tama	13-24	0.049	5.4	25.1	28.4	3.3	1.13	1.0	5.9
57	Nobles	Clarion	1-12	0.270	5.8	25.9	28.5	2.6	1.10	0.7	5.9
63	Rice	Carrington	7-12	0.278	5.3	28.2	32.5	4.3	1.15	0.1	1.3
78	Lac qui Parle	Barnes	25-36	0.093	8.0	31.9	35.6	3.7	1.12	1.4	0.4
87	Lac qui Parle	Barnes	7-12	0.264	6.1	37.0	42.2	5.2	1.14	0.3	5.2
98	Lac qui Parle	Webster	1-6	0.521	6.5	43.8	45.5	1.7	1.04	0.0	0.3
101	Aitkin	Leafmold	1	0.588	5.3	46.9	54.1	7.2	1.15	0.1	7.3
103	Jackson	Muck	7-12	1.250	3.9	48.3	58.1	9.8	1.20	0.3	13.8
104	Jackson	Muck	24-36	0.861	5.6	49.9	49.6	-0.3	0.99	0.2	1.8
108	Aitkin	Leafmold	1	0.966	5.8	52.6	62.3	9.7	1.19	1.1	4.4
113	Aitkin	Leafmold	1	2.030	4.1	90.6	98.3	7.7	1.08	0.3	6.0

but, if not, some other designation should be found for them, because the definition of the term given by Briggs and McLane has become generally recognized.

With the coarsest sands, having moisture equivalents below 2.0, the suction value is more than twice as high as the moisture equivalent, and with soils of somewhat finer texture it is from 30 to 60 per cent higher. With the soils having moisture equivalents higher than 8.0 the ratio shows no distinct de-

TABLE 4
Comparison of authors' data with those reported by Bouyoucos

GROUP	RANGE IN MOISTURE EQUIVALENT IN GROUPS	NUMBER OF SAMPLES REPORTED		AVERAGE RATIO: SUCTION VALUE TO MOISTURE EQUIVALENT		RANGE IN RATIO: SUCTION VALUE TO MOISTURE EQUIVALENT	
		Pinckney	Bouyoucos	Pinckney	Bouyoucos	Pinckney	Bouyoucos
1	1.0-2.0	6	0	2.46	2.80-2.12
2	2.1-6.0	10	1	1.26	2.21	1.67-1.17
3	6.1-8.0	4	0	1.33	1.49-1.23
4	8.1-12.0	10	1	1.17	1.34	1.36-1.09
5	12.1-16.0	9	3	1.27	0.99	1.31-1.04	1.07-0.91
6	16.1-20.0	5	1	1.18	0.91	1.26-1.10
7	20.1-25.0	9	2	1.10	1.04	1.23-1.01	1.09-0.99
8	25.1-30.0	12	7	1.09	1.07	1.20-0.95	1.14-1.02
9	30.1-35.0	20	2	1.09	1.15	1.16-0.99	1.18-1.12
10	35.1-40.0	7	2	1.11	1.10	1.18-1.05	1.11-1.10
11	40.1-45.0	6	1	1.06	1.03	1.14-0.98
12	45.1-50.0	6	1	1.10	1.14	1.20-0.99
13	50.1-55.0	4	1	1.19	1.11	1.24-1.17
14	55.0-91.0	5	3	1.09	1.08	1.15-1.03	1.10-1.06

TABLE 5
Relation of suction value-moisture equivalent ratio to nitrogen content of the soil

GROUP I				GROUP II				GROUP III			
Reference number	N	Ratio	Moisture equivalent	Reference number	N	Ratio	Moisture equivalent	Reference number	N	Ratio	Moisture equivalent
	<i>per cent</i>				<i>per cent</i>				<i>per cent</i>		
61	.031	1.20	27.0	45	.090	1.06	21.2	53	.270	1.09	25.0
75	.031	1.03	31.4	78	.093	1.12	31.9	57	.270	1.10	25.9
77	.032	1.09	31.4	69	.126	1.07	30.7	59	.275	0.95	26.3
74	.036	1.12	31.3	71	.136	1.15	30.8	63	.273	1.15	28.2
70	.037	1.08	30.8	64	.142	1.05	29.0	49	.283	1.01	22.7
79	.038	1.14	31.9	72	.148	1.11	30.8	84	.297	1.16	34.1
65	.044	1.14	29.0	76	.151	1.16	31.4	55	.301	1.05	25.8
62	.045	1.19	27.8	90	.160	1.10	38.0	81	.314	1.04	33.1
50	.056	1.23	23.1	47	.174	1.11	21.9	67	.318	1.11	30.1
82	.057	1.00	33.1	80	.211	1.12	32.6	68	.318	1.12	30.6
92	.060	1.09	39.3	73	.220	1.05	31.1	88	.355	1.05	37.0
58	.066	1.09	26.0	46	.261	1.04	21.8	83	.400	0.99	34.1
51	.072	1.19	24.0	85	.262	1.07	35.0	86	.466	1.18	36.1
60	.076	1.14	27.0	52	.263	1.12	24.0	54	.490	1.13	25.1
48	.084	1.03	22.0	87	.264	1.14	37.0	91	.606	1.06	38.8
								89	.669	1.13	38.0

Summary

GROUP	NUMBER OF SAMPLES	RANGE IN PERCENT-AGE OF N	RATIO	
			Average	Range
I	15	.031-.084	1.12	1.03-1.23
II	15	.090-.264	1.10	1.04-1.16
III	16	.270-.669	1.08	0.95-1.18

pendence upon the texture, averaging about 1.1 for the 93 soils; 19 of these, approximately a fifth, show a ratio within the limits 1.05 to 0.95, or a departure of suction value from moisture equivalent of not more than 5 per cent. In table 4 our data are summarized in comparison with those reported by Bouyoucos (2, p. 168).

TABLE 6
Relation of suction value-moisture equivalent ratio to reaction of the soil

GROUP I				GROUP II				GROUP III			
Reference number	pH value	Ratio	Moisture equivalent	Reference number	pH value	Ratio	Moisture equivalent	Reference number	pH value	Ratio	Moisture equivalent
50	5.2	1.23	23.1	45	6.7	1.06	21.2	62	7.5	1.19	27.8
51	5.2	1.19	24.0	53	6.7	1.09	25.0	48	7.6	1.03	22.0
63	5.3	1.15	28.2	86	6.7	1.18	36.1	73	7.6	1.05	31.1
54	5.4	1.13	25.1	72	7.0	1.11	30.8	76	7.6	1.16	31.4
52	5.5	1.12	24.0	82	7.0	1.00	33.1	88	7.6	1.05	37.0
89	5.5	1.13	38.0	59	7.1	0.95	26.3	60	7.8	1.14	27.0
57	5.8	1.10	25.9	67	7.1	1.11	30.1	71	7.8	1.15	30.8
56	5.9	0.99	25.9	68	7.1	1.12	30.6	80	7.8	1.12	32.6
46	6.0	1.04	21.8	58	7.2	1.09	26.0	77	7.9	1.09	31.4
55	6.0	1.05	25.8	79	7.2	1.14	31.9	65	8.0	1.14	29.0
47	6.1	1.11	21.9	91	7.2	1.06	38.8	74	8.0	1.12	31.3
87	6.1	1.14	37.0	83	7.3	0.99	34.1	78	8.0	1.12	31.9
81	6.2	1.04	33.1	90	7.3	1.10	38.0	92	8.0	1.09	39.3
84	6.4	1.16	34.1	64	7.4	1.05	29.0	70	8.1	1.08	30.8
49	6.6	1.01	22.7	85	7.4	1.07	35.0	75	8.1	1.03	31.4
69	6.6	1.07	30.7	61	7.5	1.20	27.0

Summary

GROUP	NUMBER OF SAMPLES	pH RANGE	RATIO	
			Average	Range
I	16	5.2-6.6	1.10	0.99-1.23
II	16	6.7-7.5	1.08	0.95-1.20
III	15	7.5-8.1	1.10	1.03-1.19

Duplicate determinations are far less concordant with the suction method than with the centrifuge, the average difference between duplicates for the 113 soils being 0.5 for the centrifuge and 2.3 for the suction method.

In order to bring out any relation there may be of the $\frac{\text{suction value}}{\text{moisture equivalent}}$ to either the organic matter content or the reaction, all the soils having moisture equivalents between 20 and 40 have been arranged in table 5 in order of increasing nitrogen content and in table 6 in order of rising pH value. Nitrogen was determined by the Kjeldahl method, and the reaction, by means of a pH meter using a glass electrode. No dependence of the ratio upon the nitro-

gen content is to be seen. For the present purposes the organic matter may be assumed to vary as the nitrogen, being about 20 times as high as the latter in the surface soils and somewhat lower in the subsurface samples. Of the 46 soils 16 are from the surface 1 to 6 inches, 9 from the second 6 inches, 9 from the second foot, and the 13 others from the third, fourth, fifth, or sixth foot. A similar lack of dependence of the ratio upon the reaction is seen in table 6. The average ratio is 1.10 for the most acid group of 16, with pH values between 5.2 and 6.6, as well as for the alkaline group of 15, with pH values from 7.5 to 8.1.

DISCUSSION

Bouyoucos' conclusion (2) that his suction method is simple, convenient, easily available, requires no expensive equipment, and will be useful where no moisture equivalent centrifuge is available is fully justified, as is also his statement that "in some soils the two methods agree very closely, whereas in others the agreement is not so close. . . . In general the suction method tends to give somewhat higher values than the centrifuge method." We find duplicate determinations by the suction method to agree much less closely than do those with the centrifuge. This may be illustrated by the data on the 49 soils with moisture equivalents between 20 and 40:

DIFFERENCE BETWEEN DUPLICATES, IN PERCENTAGE OF WATER RETAINED	NUMBER OF SOILS WITH THIS DIFFERENCE	
	With centrifuge	By suction
0.0-0.5	35	5
0.6-1.0	12	9
1.1-2.0	2	11
2.1-4.0	0	12
4.1-6.9	0	12

For comparing the relative texture of soils within one area, as for instance the samples from different horizons of 10 to 50 soil types within one county, the suction method may prove about as satisfactory as the centrifuge; but for comparing these data with those from another area, on the samples from which the centrifuge had been used, it is less satisfactory; and for sands, unless further developed, is quite unsuitable.

In a laboratory where a moisture equivalent centrifuge and an experienced operator are available the suction method will cause delay instead of saving time and labor, except possibly where a determination on only a very few samples at one time is desired. Where persons interested in soil texture do not have convenient access to the service of a centrifuge the suction method is to be commended.

SUMMARY

In a comparison of the value obtained by Bouyoucos' proposed suction method with the moisture equivalent determined with the Briggs-McLane

centrifuge, 113 Minnesota soils were used. These ranged in moisture equivalent from 1.5 to 90.6, in nitrogen from 0.001 to 2.03 per cent, and in pH from 4.7 to 8.1. Though the relationships found are in general agreement with those reported by Bouyoucos, they do not fully support his conclusions as to the reliability and general desirability of the method.

With loams and soils of still finer texture the suction value averaged about one-tenth higher than the moisture equivalent, whereas with the individual soils it varied from practically equal to one-third higher. With the sands of coarsest texture it was twice as high, or still higher, and with soils intermediate between these and loams it was generally intermediate but widely variable. Duplicate determinations by the suction method were found much less concordant than those with the centrifuge.

Only where a moisture equivalent centrifuge is not available does the use of the suction method appear desirable, and the values so obtained should be referred to by some other designation than *moisture equivalent*.

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WILTING COEFFICIENT AND WILTING PERCENTAGE OF THREE FOREST SOILS OF THE DUKE FOREST

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Soil analyses and determinations of moisture equivalent, wilting coefficient, and wilting percentage were made in connection with studies of the edaphic factors influencing root development in three soils of the Duke Forest, Durham, North Carolina. The soils are Congaree clay loam, Georgeville clay, and Orange loam. Certain moisture relations in the three soils are clarified by the data obtained.

The Congaree clay loam area that was studied occupies the forested bottom land along Browning's Branch in Compartment 32 and 33 of the Durham Division of the Duke Forest. The area is subject to inundation but between overflows is moderately well drained. Variable amounts of alluvium are deposited with each inundation. The soil has developed only an A₁ horizon. It consists of a brown clay loam that is plastic when moist, extending to a depth of 1.5 to 2.5 inches. From that depth down to 6.5 to 10 inches is a layer of structureless sandy loam, lighter in color, largely because of a lower organic matter content. Below the latter layer are generally found stratified layers of sand and sandy loam. At a depth of 18 to 20 inches may be found residual soil, or, 3 or more additional feet of alluvial soil and then residual soil. Most of the entire soil is rather loose and contains small mica flakes.

The Georgeville clay area is in Stand 2, Compartment 15 of the New Hope Creek Division of the Forest. The area is well drained, being located on a gently rounded upland area between two small streams, and is forested with an oak-hickory wood. The Georgeville soil profile is well developed. The A₁ horizon is light brown, stony clay, passing at 0.5 to 1.5 inches into the A₂ horizon, a reddish yellow, rather compact, stony clay exhibiting a crumb structure and extending to a depth of 5 to 7 inches. The B₁ horizon is dark red, brittle clay, exhibiting bright surfaces when moist soil is broken. It gradually grades into the B₂ horizon, which is slightly darker and more compact than the B₁. The C horizon occurs at a depth of 24 to 40 inches. It is yellowish red granular clay with lighter mottlings.

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The Orange loam area is in Stand 1 of Compartment 15 of the New Hope Creek Division of the Forest. The area is upland but is poorly drained, the slope being too gentle to allow proper drainage. The forest on the area is of the post oak-blackjack oak type. The A₁ horizon is light gray, floury, stony loam, underlain at 1 to 2 inches by dull yellow loam (A₂ horizon) which extends to a depth of 7 to 9 inches. The B horizon is dingy yellow, extremely plastic, waxy, impervious clay. The C horizon, which begins at 17 to 20 inches, is friable, mixed green and yellow clay.

METHODS OF STUDY

Following preliminary examination with a soil auger, three locations were selected as typical of each area. At each location a profile was dug, and duplicate pint samples of soil were taken from each soil horizon by means of a soil sampler devised to take samples of undisturbed soil for making determinations of wilting percentage (4). At regularly spaced intervals near the center of each area, 20 samples in duplicate were taken from the surface horizon. The subsurface soil samples were taken as the soil profiles were dug. The soil from each profile was removed to the desired depth for sampling (2 inches, 10 inches, and 24 inches). At regular intervals across the exposed surface three samples in duplicate were taken from each profile.

A second set of samples was collected in loose condition from the profiles, 2 quarts being taken from each horizon. These samples were brought into the laboratory, dried, and crushed with a wooden rolling pin so as to break up the soil aggregates and enable them to pass through a 2-mm. sieve. Soil particles that did not pass through the sieve openings were classified as gravel. The portion of the soil that passed through the sieve was then thoroughly mixed and all but 1 quart discarded. In each soil a composite sample was then made for each horizon by combining samples from the profiles. The composite samples were used for mechanical analyses, which were made in duplicate by a modification of Olmstead's (7) pipette method. The textural class for each horizon was determined by the equilateral triangle method of Davis and Bennett (6).

The samples for determination of the wilting percentage were obtained in cardboard containers that had been boiled in paraffin to make them moisture-proof. One series of these duplicate pint samples was used in the determination of the wilting percentage. The procedure for the determination of the lower limit of available soil moisture as outlined and discussed by Briggs and Shantz (1, 3) was used as a basis for determination of the wilting percentage. All soil down to within 1.5 inches of the top of each container was removed, leaving a sample approximately 1.5 inches thick in each can. The soil in the containers was saturated with tap water, and germinating oat (*Avena sativa* L.) seeds were placed on the surface. These seeds were covered with approximately one-fourth inch of dry, finely divided soil taken from the portion of soil that had been removed from the top. This covering of soil was allowed to

become moistened by capillary rise of water from the saturated soil below. The samples were placed in the Duke University greenhouse. The surface of the soil was kept moist by additions of small amounts of water until the plants had become well established and the moisture content of the soil below the surface had been reduced to near the wilting percentage. At that time the surface of the soil was sealed with paraffin to a depth of about 5 mm. When the oats were permanently wilted the moisture content was determined for the entire soil sample except that part which had been used as a cover for the oats seeds.

Oats were used as phytometers because previous experiments conducted in the Duke University greenhouse showed that good growth of root and tops is obtained from them and their wilting point can be easily ascertained. The work of Veihmeyer and Hendrickson (8, 9, 10) indicates that any small plant grown in a sealed container may be used as an indicator of the minimum available moisture content.

The second series of pint samples was used to determine moisture equivalent. The samples were carefully removed from the containers, and blocks of soil one-half inch thick were cut to fit the moisture equivalent pans. One block was cut from the upper part of a sample and another 1 inch from the bottom of the first block. Data from these determinations are designated as "moisture equivalent in place" for each particular depth in the soil profile from which the one-half inch thick soil samples were taken. The remainder of each pint sample was rolled and run through a 2-mm. sieve. The gravel was discarded. The portion that passed through the sieve was then thoroughly mixed, and duplicate samples were taken for determining the moisture equivalent of the sieved soil. The usual procedure in determining the moisture equivalent as given by Veihmeyer, Israelson, and Conrad (12) was followed. The wilting coefficient values for the samples were determined from the moisture equivalent values in place. The relationship between the moisture equivalent and the wilting coefficient of soils as developed by Briggs and Shantz (2) was used to determine the wilting coefficients.

RESULTS

The results of the mechanical analyses of the Congaree, Georgeville, and Orange soils are presented in table 1. On the basis of the texture of the A_1 horizon it is apparent that the Congaree soil is classed as a clay loam, the Georgeville as a clay, and the Orange as a loam.

The profile of the Congaree soil is almost entirely free of gravel. In the A horizons of the Georgeville and the A_2 horizon of the Orange the gravel constitutes approximately one-fourth of the total weight of soil. The other horizons in the latter two soils are less gravelly. The Georgeville soil contains more gravel throughout the profile than the other two soils.

In regard to the other soil fractions, the Congaree is characterized by relatively large percentages of sand and small amounts of colloids at all depths

and by a decreasing clay content with increased depth. The high sand content of horizon 4 should be noted. Both the A horizons of the Georgeville soil are composed of approximately equal amounts of total sands, silt, and clay. The B horizons are very high in clay content and percentage of colloids. In the Orange soil the A horizons are composed largely of equal amounts of total sands and silt, whereas the B horizons are composed of about 50 per cent clay.

If all the means of the moisture equivalent determinations made at the various depths are considered, a rather complete picture is obtained of moisture equivalent values throughout most of each of the three soil profiles. The

TABLE 1

Results, in percentage of oven-dry weight, of mechanical analyses of Congaree, Georgeville, and Orange soils determined by the pipette method

HORIZON	DEPTH, INCHES	GRAVEL	TOTAL SANDS	SILT	CLAY	COLLOIDS	TEXTURAL GRADE
<i>Congaree soil</i>							
A ₁	0-2	None	38.42	37.81	23.77	15.68	Clay loam
2	2-7.5	None	57.75	24.45	17.00	14.74	Sandy loam
3	7.5-19	Trace	58.21	25.49	16.30	11.54	Sandy loam
4	19-25	Trace	84.80	8.81	6.39	4.26	Sand
5	Below 25	None	57.36	27.78	14.86	10.32	Sandy loam
<i>Georgeville soil</i>							
A ₁	0-1.2	27.96	29.33	38.11	32.56	21.60	Clay
A ₂	1.2-6	22.78	27.85	37.22	34.93	26.00	Clay
B ₁	6-20	9.32	10.77	16.51	72.72	70.53	Clay
B ₂	20-33	4.85	9.15	22.36	68.49	64.96	Clay
C	Below 33	Trace	17.05	31.69	51.26	41.98	Clay
<i>Orange soil</i>							
A ₁	0-1.5	4.78	40.64	43.98	15.38	11.02	Loam
A ₂	1.5-8	27.07	42.94	38.76	18.30	15.46	Loam
B ₁	8-14	3.18	18.71	30.39	50.90	46.38	Clay
B ₂	14-19	1.47	21.51	30.67	47.82	40.80	Clay
C	Below 19	1.79	35.98	34.00	30.02	26.36	Clay

results are presented in table 2. It is evident that the moisture equivalent values are high near the surface of the soils.

In the Congaree profile the values drop off rapidly with increasing depth, reaching a minimum in horizon 3 at a depth of 12 to 16 inches. The values are slightly higher in horizons 4 and 5 but are still relatively low. The fact that the amounts of colloids determined by the pipette method (table 1) are increasingly smaller until the lowest horizon is reached, where the amount increases again, partly accounts for the moisture equivalent values that were obtained, because soils with high percentages of the smaller soil fractions retain more moisture when centrifuged than do those with low percentages.

In the Georgeville profile the moisture equivalent drops to a minimum in the A₂ horizon at a depth of approximately 2 to 4 inches but because of the extremely high amount of colloids in the B horizons, the moisture equivalent rises to a high level. The maximum moisture equivalent, 38 per cent, is at a depth of 23 inches.

In the Orange profile approximately the same situation exists as in the Georgeville. The moisture equivalents, however, are generally lower, as might be expected upon consideration of the amounts of colloids (table 1), which are correspondingly lower.

TABLE 2

Mean moisture equivalents with standard errors determined from pint samples taken at the depths indicated in the Congaree, Georgeville, and Orange soil profiles

SAMPLE	CONGAREE	GEORGEVILLE	ORANGE
Surface* (0-3 inches)			
In place (top).....	33.56 \pm 0.98	26.70 \pm 0.54	21.46 \pm 0.77
In place (1.5 inches).....	25.87 \pm 0.34	21.60 \pm 0.40	13.66 \pm 0.25
Sieved.....	24.92 \pm 0.25	26.69 \pm 0.32	23.31 \pm 0.25
2-5 inches†			
In place (top).....	22.12 \pm 0.57	20.01 \pm 0.64	13.62 \pm 0.18
In place (1.5 inches).....	20.06 \pm 0.78	21.18 \pm 0.35	12.94 \pm 0.17
Sieved.....	18.44 \pm 0.65	23.80 \pm 0.31	13.91 \pm 0.09
10-13 inches†			
In place (top).....	14.02 \pm 1.17	32.24 \pm 1.41	22.70 \pm 0.71
In place (1.5 inches).....	11.26 \pm 0.56	32.67 \pm 1.33	25.10 \pm 0.73
Sieved.....	11.83 \pm 0.83	34.32 \pm 1.31	28.61 \pm 1.39
23-27 inches†			
In place (top).....	14.11 \pm 0.81	38.00 \pm 1.36
In place (1.5 inches).....	14.13 \pm 0.50	36.38 \pm 1.53
Sieved.....	14.17 \pm 0.77	37.97 \pm 1.24

* 20 determinations on each area for every mean.

† 9 determinations on each area for every mean.

Duplicate determinations of the organic matter in the soil horizons showed that the surface soils contain a higher percentage than other horizons and that the amount decreases with increasing depth. The presence of the larger amounts of organic matter in the surface soils may account for at least part of the increased moisture equivalents at the surface, since the amounts of colloids in the A₂ horizons are approximately the same as at the surface and therefore likely do not cause the differences.

Throughout the Georgeville and Orange soil profiles the values obtained from the undisturbed soil are slightly lower than the values from sieved soil. This agrees with results obtained by Davis and Adams (5), who found that blocks of undisturbed soil give slightly lower moisture equivalent values than do crushed samples of the same material. Very likely the following conditions

obtain in regard to the two soil profiles. The undisturbed soil is apparently structurally arranged so that small drainage passages exist and allow better drainage of the water during centrifuging than that of the sieved soil, which has had the passages broken up. The removal of gravel from the sieved soil also may have brought about an increase in values for the sieved soil.

The two sets of moisture equivalent values in the Congaree profile differ very little; the values obtained from the sieved soil of the upper horizons being only slightly lower than those from undisturbed soil. This is the reverse of the situation in the Orange and Georgeville soil profiles. There are apparently

TABLE 3

Mean wilting percentages with standard errors, wilting coefficients, and ratio of moisture equivalent to wilting percentage in the Congaree, Georgeville, and Orange soils at the depths indicated

SAMPLE	CONGAREE	GEORGEVILLE	ORANGE
Surface (0-1.5 inches)			
Wilting percentage*.....	7.68 \pm 0.23	6.16 \pm 0.31	4.31 \pm 0.21
Wilting coefficient.....	16.25	13.64	10.11
Ratio†.....	3.89	4.07	4.32
2-3.5 inches			
Wilting percentage‡.....	5.34 \pm 0.63	5.54 \pm 0.43	3.03 \pm 0.08
Wilting coefficient.....	11.68	10.76	7.01
Ratio‡.....	4.03	3.57	4.26
10-11.5 inches			
Wilting percentage‡.....	2.24 \pm 0.33	20.51 \pm 1.12	10.41 \pm 0.51
Wilting coefficient.....	6.88	17.47	12.72
Ratio‡.....	5.65	1.57	2.25
23-24.5 inches			
Wilting percentage‡.....	4.58 \pm 0.61	22.85 \pm 1.27
Wilting coefficient.....	7.58	20.54
Ratio‡.....	3.05	1.65

* 20 determinations on each area for every mean.

† Ratio is moisture equivalent divided by wilting percentage.

‡ 9 determinations on each area for every mean.

few drainage passages as a result of structural arrangement of the particles in the Congaree soil, and therefore when the soil aggregates are partly broken up better drainage of water occurs through the soil, because the coarse texture of the Congaree soil allows a smaller amount of compaction on centrifuging than in the two fine-textured soils.

The results of the determinations of the wilting percentages are presented in table 3. The wilting percentages of all horizons follow the general trend of the moisture equivalent values. In the Congaree soil profile the A₁ horizon

has the highest wilting percentage. In horizon 3 the minimum value is found, and this increases gradually in horizons 4 and 5. The whole general trend throughout the profile is probably a result of the same factors that influence moisture equivalent values. This is probably true of the Georgeville and Orange profiles as well.

In order to have wilting coefficients for exactly the same depths as the average depth of the samples from which the wilting percentages were determined, moisture equivalent values were estimated from curves of moisture equivalent in place. The estimated values were used to calculate the wilting coefficients which are presented in table 3. The moisture equivalents were also divided by the wilting percentages, and the ratios are presented in the same table. The ratio of the moisture equivalent to the wilting percentage varies from 1.57 to 5.65 and therefore does not agree with the determinations of Briggs and Shantz (2) on other soils, where the ratio was found to be approximately 1.84. No reason for this wide difference can be given on the basis of the data obtained in this study. The data of Veihmeyer and Hendrickson (9) show that the residual moisture at permanent wilting cannot be obtained in every case from the moisture equivalent by use of the factor 1.84. They found ratios from 1.73 to 3.82. From the differences that exist between the wilting percentage and wilting coefficient values in the present study it is apparent that the wilting coefficient is not a good measure of the lower limit of available water in the three forest soils, Congaree clay loam, Georgeville clay, and Orange loam.

SUMMARY

Soil analyses and determinations of moisture equivalent, wilting coefficient, and wilting percentage were made of three forest soils of the Duke Forest, Congaree clay loam, Georgeville clay, and Orange loam.

Each of the experimental areas is described briefly.

Experimental methods are described.

Moisture equivalent values were found to be higher in sieved than in unsieved soil in the Georgeville and Orange soils.

Moisture equivalent values for the lower soil horizons appear to be directly correlated with colloid content. Organic content appears to be directly correlated with the values for the surface horizons.

Wilting percentages, though much lower, were found to follow the general trend of the moisture equivalent values. The wilting percentage values are apparently conditioned by the same factors that influence the moisture equivalent values.

The ratio of moisture equivalent to wilting percentage was found to vary from 1.57 to 5.65.

Wilting coefficient values were found to vary considerably from those of the wilting percentage. Wilting coefficient, therefore, is not a good measure of the lower limit of available water in Congaree clay loam, Georgeville clay, and Orange loam soils of the Duke Forest.

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THE INFLUENCE OF CROPPING PRACTICES ON SOME PHYSICAL AND CHEMICAL PROPERTIES OF SOIL¹

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The soil conservation program for the Piedmont Plateau includes the use of close-growing crops, chiefly legumes such as Austrian winter peas, crimson clover, vetch, soybeans, and lespedeza, as an effective means for the control of sheet erosion on terraced lands. The protection afforded by these crops may be attributed to a combination of factors such as the interception of rainfall by the vegetative covering, the mechanical effect of plants and plant roots, and the alteration of the structure of the soil.

Data presented by Middleton, et al. (12, 13), Peele and Moser (17), and Diseker and Yoder (6) showed that soil and water losses from cultivable areas were materially reduced when legume crops were included in the rotation. Haynes³ has shown that the maximum interception of rainfall by the plant canopy is reached as the plant approaches maturity. Lyon and Buckman (10, p. 48-52) point out that organic matter plays an important role in the formation of a desirable soil structure by increasing the porosity and absorptive capacity, by improving the tilth through the formation of a crumb structure, and by developing larger aggregates.

Until recently, only meager quantitative data were available on the relationship between physical properties of soil and its erodibility. Data reported by Musgrave (15), Baver (2), Browning (5), and Peele (16) showed that organic matter increased percolation and aided in formation of larger stable aggregates. Musgrave (15) suggested, however, that organic matter may not always increase the rate of water movement through soil, for in the Upshur soil organic matter reduced the rate of water movement. His hypothesis is that the retardation in this soil was due to the presence of active inorganic colloids. A decrease in percolation was also reported by Lyon et al. (9), in lysimeter experiments on Dunkirk silty clay loam. The tanks without legumes

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³ Haynes, J. L. 1937 Interception of rainfall by vegetative canopy. Mimeograph. Cir. of Symposium of Vegetative Method of Erosion Control. Ann. Meeting Amer. Soc. Agron.

in the rotation gave higher percolation rates than did the tanks with legumes in the rotation.

EROSION LOSSES MEASURED UNDER FIELD CONDITIONS

Differences in soil and water losses resulting from various cropping systems were obtained from erosion control plats on Cecil sandy clay loam at Tigerville, Duncan, and Greer, South Carolina. These experiments were designed

TABLE 1

Monthly rainfall, run-off, and soil loss under different cropping systems designed for erosion control on Cecil sandy clay loam at Tigerville, S. C.

MONTH	RAINFALL	CROPPING SYSTEM							
		Corn-cotton		Corn-cotton-(vetch)		Oats-(lespedeza)-cotton		Fallow	
		Run-off	Soil loss	Run-off	Soil loss	Run-off	Soil loss	Run-off	Soil loss
	<i>inches</i>	<i>per cent</i>	<i>tons/A.</i>	<i>per cent</i>	<i>tons/A.</i>	<i>per cent</i>	<i>tons/A.</i>	<i>per cent</i>	<i>tons/A.</i>
1937									
January.....	11.67	32.59	0.60	19.42	0.09	0.67	0.00	30.67	1.21
February.....	3.95	8.59	0.24	5.98	0.04	0.27	0.00	5.12	0.20
March.....	2.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
April.....	5.47	7.33	0.03	4.21	0.01	2.61	0.01	21.57	4.18
May.....	3.18	10.43	0.16	3.95	0.02	9.60	2.04	37.32	10.12
June.....	3.44	18.16	4.91	13.09	2.54	17.48	5.19	36.99	14.89
July.....	5.40	24.19	4.93	18.99	2.34	12.35	1.97	28.40	9.72
August.....	8.65	41.59	9.12	38.26	5.01	26.50	3.43	40.50	14.60
September.....	4.56	60.09	1.90	46.18	1.97	32.00	0.38	40.62	10.32
October.....	9.08	41.47	0.44	4.72	0.03	1.01	0.00	39.50	0.54
November.....	1.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
December.....	2.35	0.02	0.00	0.00	0.00	0.04	0.00	0.12	0.00
1938									
January.....	3.24	0.39	0.00	0.03	0.00	0.12	0.00	0.78	0.01
February.....	1.96	0.05	0.00	0.00	0.00	0.10	0.00	0.10	0.00
March.....	6.07	8.12	0.11	0.48	0.00	7.16	0.14	25.20	6.78
April.....	2.25	1.59	0.00	0.08	0.00	1.34	0.00	6.01	0.11
May.....	4.40	0.19	0.00	0.19	0.00	8.60	0.05	24.59	5.27
June.....	3.49	0.39	0.00	0.36	0.00	7.05	0.12	10.45	3.50
Total.....	82.32	19.98	22.44	12.28	12.05	8.10	13.33	25.20	81.45

to collect the soil and water eroding from 1/100-acre plats. Suitable calibrated catchment tanks were placed at the bottom of each plat for this purpose. After each rain the amount of run-off was measured, and an aliquot of the eroded material was brought to the laboratory to determine the total soil loss from each rotation. Monthly summaries of rainfall and soil and water losses for the erosion control plats under various cropping systems are presented in tables 1, 2, and 3. The average run-off (table 4) shows significant differences for various cropping systems, but does not show the comparative amounts of

erosion occurring under the different rotations. The results from the Tigerville experiment show that erosion was markedly reduced during periods when the legumes afforded the maximum cover. In the oats-(lespedeza)-cotton rotation, the run-off and soil losses were highest during the early part of the first season when lespedeza was becoming established, but were almost nil during the latter part of the season and throughout the entire second season. The vetch cover crop had a similar retarding effect on erosion except that the

TABLE 2

Monthly rainfall, run-off, and soil loss under different cropping systems designed for erosion control on Cecil sandy clay loam at Duncan, S. C.

MONTH	RAINFALL	CROPPING SYSTEM							
		Corn-cotton		Oats-(lespedeza)-cotton		Oats-(soybeans)-cotton		Fallow	
		Run-off	Soil loss	Run-off	Soil loss	Run-off	Soil loss	Run-off	Soil loss
	<i>inches</i>	<i>per cent</i>	<i>tons/A.</i>	<i>per cent</i>	<i>tons/A.</i>	<i>per cent</i>	<i>tons/A.</i>	<i>per cent</i>	<i>tons/A.</i>
1937									
January.....	10.73	34.94	0.22	34.32	0.55	8.54	0.02	36.76	0.58
February.....	3.59	5.20	0.01	6.18	0.08	0.60	0.00	8.53	0.09
March.....	2.25	0.42	0.00	0.24	0.00	0.00	0.00	0.20	0.00
April.....	5.65	4.80	0.03	13.67	0.11	8.51	0.08	15.96	1.33
May.....	3.71	2.66	0.02	25.83	0.22	26.23	0.58	33.76	0.52
June.....	6.50	42.87	18.44	54.53	0.28	45.70	21.55	61.88	19.01
July.....	2.88	27.52	0.86	19.11	0.15	15.53	2.30	29.61	6.55
August.....	4.33	24.09	0.39	9.55	0.01	17.39	0.30	22.06	1.20
September.....	3.92	49.09	0.57	31.70	0.00	43.57	0.33	43.33	4.35
October.....	10.66	46.49	0.88	16.47	0.00	32.12	0.26	42.28	1.26
November.....	1.29	0.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00
December.....	2.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1938									
January.....	2.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
February.....	1.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
March.....	3.27	2.51	0.01	0.12	0.00	0.18	0.00	5.99	0.05
April.....	2.02	0.34	0.00	0.06	0.00	0.06	0.00	5.46	0.01
May.....	2.89	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00
June.....	2.47	18.31	0.36	0.66	0.00	15.60	0.58	32.86	2.28
Total.....	71.94	22.81	21.79	18.31	1.40	16.80	26.00	27.09	37.23

cultivation of the soil required in seeding the crop was partly responsible for the low erosion losses in September. After the crop was established, a marked reduction in erosion occurred, and soil and water losses were almost negligible during the period of maximum growth.

The effects of legumes on erosion control were not so pronounced at Duncan (table 2) as at Tigerville. The oats-(lespedeza)-cotton rotation was started after the outset of the experiment, and very low amounts of rainfall occurred during the effective growth period for lespedeza, which is normally the second

year. As a result, the run-off differences were not so pronounced as they would probably have been if a normal amount of precipitation had occurred during the first 6 months of 1938.

The effects of the legume at Duncan and Greer were also minimized by the initial high organic matter content of this soil, as lespedeza had been included in the crop rotation practiced on the field several years before the control plats were established. The legume plats in both of these experiments, however, gave a reduced soil and water loss in comparison with the non legume

TABLE 3

Monthly rainfall, run-off, and soil loss under different cropping systems designed for erosion control on Cecil sandy clay loam at Greer, S. C.

MONTH	RAIN- FALL	CROPPING SYSTEM									
		Corn-cotton		Corn-cotton-(vetch)		Oats-(lespedeza)-cotton		Oats-(soybeans)-cotton		Fallow	
		Run-off	Soil loss	Run-off	Soil loss	Run-off	Soil loss	Run-off	Soil loss	Run-off	Soil loss
	inches	per cent	tons/A.	per cent	tons/A.	per cent	tons/A.	per cent	tons/A.	per cent	tons/A.
1937											
April.....	6.15	3.32	0.06	2.81	0.03	13.22	1.18	13.63	1.56	25.89	2.10
May.....	3.59	5.91	0.04	3.31	0.01	27.79	0.13	28.40	0.22	39.52	0.38
June.....	6.55	48.83	2.59	47.47	2.32	49.50	0.72	52.45	0.93	66.15	6.96
July.....	2.71	13.14	0.19	9.12	0.02	17.02	0.13	8.08	0.35	27.61	3.06
August.....	4.94	22.15	0.07	13.32	0.06	18.87	0.13	17.87	0.12	40.80	0.57
September.....	4.50	41.94	0.12	49.14	0.16	45.33	0.07	48.40	0.22	56.90	3.84
October.....	10.91	29.97	0.08	21.08	0.15	23.26	0.02	20.21	0.06	57.85	2.67
November.....	1.47	0.86	0.00	0.53	0.00	0.92	0.00	0.59	0.00	0.79	0.00
December.....	2.26	1.00	0.00	1.06	0.00	0.81	0.00	0.77	0.00	0.26	0.00
1938											
January.....	2.82	1.74	0.00	2.43	0.00	1.32	0.00	1.24	0.00	1.31	0.00
February.....	1.19	0.89	0.00	0.48	0.00	0.77	0.00	0.65	0.00	0.08	0.00
March.....	3.59	2.45	0.00	1.38	0.00	1.60	0.00	2.28	0.02	13.19	0.40
April.....	2.23	0.26	0.00	0.22	0.00	1.48	0.00	0.80	0.00	2.09	0.00
May.....	3.44	0.37	0.00	0.22	0.00	1.39	0.00	0.28	0.00	9.31	0.10
June.....	2.47	3.85	0.02	5.86	0.02	1.85	0.00	5.67	0.04	20.17	0.18
Total.....	58.82	16.31	3.17	13.60	2.77	14.17	2.38	13.64	3.52	16.35	20.26

plat, but the differences were more pronounced during the period when the plats provided the maximum cover.

The oats-(soybeans)-cotton rotation system afforded some protection, but was not nearly so effective as the cropping practice including either lespedeza or vetch. The soil planted to the oats-(soybeans)-cotton rotation eroded more readily during the early growth stage of the soybeans than was the case in the the corn-cotton rotation, but a reduced erosion loss occurred during the late fall and winter months. Apparently some differences occurred in soil structure, as there was less erosion during the following season. Some of the

beneficial effects of the soybeans may have been due to the fissures in the soil formed by the taproots.

The data from these experiments show not only that the erosion losses were retarded during the actual growing periods of the legumes, but that the soil

TABLE 4.

Influence of various cropping systems on soil properties associated with water movement and average annual run-off

LOCATION	CROPPING SYSTEM	ORGANIC MATTER	HUMUS	PERCOLATION	RUN-OFF	AGGREGATE SIZES				
						1.0 mm.	1.0-0.5 mm.	0.5-0.05 mm.	0.05-0.02 mm.	<0.02 mm.
		per cent	per cent	in./hr.	per cent	per cent	per cent	per cent	per cent	per cent
Tigerville	Before cropping*	1.20	0.18	10.92	7.43	19.25	58.42	5.03	9.87
	Corn-cotton	1.18	0.17	5.13	19.85	8.10	17.20	58.00	7.30	9.40
	Corn-cotton-(vetch)	1.46	0.23	12.52	15.09	12.71	21.17	53.22	7.90	5.10
	Oats-(lespedeza)-cotton	1.48	0.23	7.94	6.58	10.02	19.55	56.93	7.05	7.45
	Bermuda sod	2.76	0.61	12.28	0.16	17.87	22.25	47.38	9.20	4.40
	Fallow	1.10	0.11	10.73	30.25	12.22	22.39	53.37	5.50	6.00
Duncan	Before cropping*	2.10	0.12	11.98	8.97	12.48	66.65	8.37	4.53
	Corn-cotton	2.09	0.14	12.27	27.02	18.50	17.25	52.56	6.91	4.77
	Oats-(lespedeza)-cotton	2.43	0.21	12.21	19.52	15.34	13.92	60.68	6.80	4.26
	Oats-(soybeans)-cotton	2.05	0.13	13.87	23.71	12.35	13.31	64.04	5.47	4.87
	Bermuda sod	2.45	0.45	12.18	0.42	20.10	18.72	51.88	4.74	4.65
	Fallow	1.56	0.12	10.83	31.22	10.46	12.17	64.53	8.18	4.78
Greer	Before cropping*	2.52	0.21	10.61	12.02	18.21	56.77	5.44	7.66
	Corn-cotton	2.53	0.22	12.18	16.31	19.00	16.01	50.99	5.44	8.87
	Corn-cotton-(vetch)	2.61	0.27	15.62	13.60	21.57	20.76	45.17	6.05	6.05
	Oats-(lespedeza)-cotton	2.70	0.27	12.82	14.17	17.01	18.99	52.36	6.37	6.37
	Oats-(soybeans)-cotton	2.57	0.24	10.86	13.64	21.42	19.31	47.25	5.35	6.47
	Fallow	2.52	0.21	12.18	30.64	16.35	14.75	53.94	8.19	6.87
Clemson	Cotton	1.23	0.11	13.42	7.00	27.72	48.90	7.16	9.22
	Cotton (vetch)	1.72	0.24	18.20	7.53	25.73	54.68	7.21	4.85
	Cotton, 8 T. manure	1.76	0.23	16.86	9.31	27.58	52.52	6.35	4.44
	Cotton-(vetch), 8 T. manure	1.87	0.22	17.27	6.20	32.65	49.63	7.03	4.62

* Data represent analyses of original soil.

was less susceptible to erosion during the succeeding year when cultivated crops were growing. These differences suggested that an investigation of certain physical properties of these soils might give some additional information on the soil structure which persists in the soil after the cover crop has been turned under as green manure.

EXPERIMENTAL PROCEDURE

Soil samples were taken at the outset and at the end of the experiment from each of the erosion control plats, and also from certain plats at Clemson designed to study crop responses from additions of organic matter applied in the form of barnyard manure and from vetch as green manure. These samples were taken to the laboratory to determine the chemical and physical differences associated with erodibility of soils under field conditions.

The amount of organic carbon was determined by the dry combustion method (1, p. 4), and the results were converted into organic matter by multiplying by the factor 1.724; the humus content was obtained by extraction with a 2.5 per cent NaOH solution followed by precipitation with HCl according to the method of Waksman (20). Analyses of the soil aggregates were made by a modification of the method outlined by Bouyoucos (3). After passing through the 0.5-mm. sieve, the soil suspension was transferred to a hydrometer jar. The readings with a Bouyoucos soil hydrometer were made at various time intervals corresponding to settling velocities of various sized particles as calculated by the Stokes formula. Mechanical analysis was determined by the pipette method of Olmstead, et al. (14), moisture equivalent by the method of Briggs and McLane (4), and saturation capacity by the method of Keen and Raczkowski (7).

Field volume weight, or apparent specific gravity, was determined by the procedure of King (8), field capacity moisture by the method inaugurated by Shaw (18), and percolation was determined in artificial packed tubes, being expressed in inches per hour according to the formula of Slater and Byers (19). The volume of macropores was calculated by computing the total pore space by the usual method and subtracting the volume occupied by the micropores, which was calculated by multiplying the moisture equivalent by the volume weight of the soil.

SOIL PROPERTIES AS AFFECTED BY CROPS

A comparison of the organic matter, humus content, rate of percolation, and size of aggregates is shown in table 4 together with the run-off percentage under field conditions. The organic matter content at the outset of the experiment at Tigerville was 1.20 per cent, at Duncan 2.10 per cent, and at Greer 2.52 per cent. At Tigerville, appreciable changes have occurred during the experiment under the various cropping systems. Lespedeza and vetch were effective in increasing the organic matter content, while a gradual depletion of organic matter occurred in the fallow plat. At Duncan, the same general effects resulted from identical cropping systems. Bermuda grass had the most influence on increasing the content of organic matter, while soybeans maintained a level approximately at the initial amount. Since the soybeans were removed as hay no marked increase was expected. At Greer the effects of the legumes were somewhat minimized, probably because of the high initial

level of organic matter; however, the soil-conserving rotations showed slight increases when compared with either the fallow plat or the corn-cotton rotation.

The results from certain plats at Clemson were also included with these data in order to obtain the cumulative effects of 12 annual applications of stable manure, manure plus a vetch cover crop, and vetch turned under as green manure upon physical properties of the soil. The percentage of organic matter in the soil from the manure and vetch plats was higher than that in the soil from the continuous cotton plat.

The effects of the various crops on soil aggregation show some differences. The data from the Tigerville and Clemson plats are probably more significant than those from the other locations, as these experiments had been in progress for a longer time. The differences in percentages of various sized aggregates are more evident in the <0.02 -mm. size than in the other divisions. At Tigerville, a lower percentage of small aggregates, with the exception of the fallow soil, and a higher percentage of 0.05 – 0.02 -mm. particles were found in the soil from the Bermuda grass sod than in the other soils. Lespedeza and vetch were not quite so effective in the formation of soil aggregates as was the Bermuda grass, but a lower percentage of particles <0.02 mm. was found in the soil from the rotations including these legumes than from the nonlegume rotation. The effects of crops on aggregate formation were somewhat nullified in the Duncan and Greer experiments by the higher organic matter levels of these two soils. As a consequence, the percentage of particles <0.02 mm. was almost identical on all cropped plats. Metzger and Hyde (11) in their recent work suggested that organic matter encourages soil aggregation.

The fallow plat at Tigerville showed a lower percentage of aggregates in the 0.05 – 0.02 -mm. range than did any of the cropped soils, a result which was contrary to the relation between organic matter and soil aggregation. Erosion in this case had removed the major portion of the surface soil, and the upper $6\frac{3}{4}$ inches of soil contained a considerable amount of the B horizon. Mechanical analysis of the soil showed that the clay content was higher in the fallow plat at the end than at the outset of the experiment. As subsurface soils usually are more highly aggregated than surface soils, a lower percentage of aggregates <0.02 mm. would be anticipated in the fallow plat.

Some irregularities appeared in the percolation rate. This may be influenced by numerous factors, among which the nature and extent of the organic matter are extremely important. The humus content was determined to obtain some idea of the relative amounts of the finely divided organic colloidal material, since the determination of total organic matter does not show the chemical nature of the material. The variation in content of humus was not so great as that found in total organic matter, which appeared to be associated with the type of plant material applied to the soil. Generally the run-off was high and the percolation rate was low where the humus content was low, whereas the run-off was lower and the percolation rate higher where the humus content was high. Apparently, percolation rates as determined in this experiment

TABLE 5

Influence of various cropping systems on certain physical properties associated with erodibility of soils

LOCATION	CROPPING SYSTEM	VOLUME WEIGHT	WATER AT SATURATION	FIELD MOISTURE CAPACITY	MOISTURE EQUIVALENT	SUSPENSION PERCENT-AGE (0.02 MM.)	VOLUME OF MACRO-PORES	DISPERSION RATIO (0.02 MM.)	MECHANICAL ANALYSIS		
			per cent			per cent			Sand	Silt	Clay
Tigerville	Before cropping*	1.19	35.36	15.89	5.27	36.19	14.69	65.91	11.82	22.27
	Corn-cotton	1.20	34.41	15.51	15.26	7.65	36.42	22.08	65.35	12.09	22.56
	Corn-cotton-(vetch)	1.16	36.48	17.61	15.45	5.32	38.45	15.63	65.91	11.55	22.54
	Oats-(lespedeza)-cotton	1.13	40.70	17.22	16.08	5.93	39.19	15.98	62.90	13.24	23.86
	Bermuda sod	1.12	37.37	20.42	17.70	5.65	36.81	15.79	64.25	14.58	21.17
	Fallow	1.26	32.47	15.36	16.11	6.04	23.24	15.94	62.11	13.83	24.06
Duncan	Before cropping*	1.25	45.21	15.70	3.59	33.22	11.19	70.56	10.48	19.94
	Corn-cotton	1.22	47.38	12.28	15.20	5.77	35.74	18.96	69.58	8.93	21.49
	Oats-(lespedeza)-cotton	1.16	47.74	15.65	16.14	4.84	38.08	16.56	70.64	8.23	21.13
	Oats-(soybeans)-cotton	1.26	45.65	13.08	15.47	5.04	32.97	16.54	69.54	11.29	19.17
	Bermuda sod	1.17	48.83	15.78	15.20	4.22	37.87	17.40	75.75	10.43	13.82
	Fallow	1.35	44.56	12.05	14.38	5.85	29.67	24.90	76.51	9.88	13.61
Greer	Before cropping*	1.24	35.47	14.30	4.40	35.48	13.99	71.73	10.75	17.52
	Corn-cotton	1.25	31.58	12.12	12.61	4.81	37.07	21.06	77.16	11.02	11.82
	Corn-cotton-(vetch)	1.24	32.57	13.37	12.57	3.11	37.62	14.45	78.47	11.27	10.26
	Oats-(lespedeza)-cotton	1.20	38.03	17.70	15.01	5.33	36.71	15.56	65.74	12.01	22.24
	Oats-(soybeans)-cotton	1.19	35.85	13.71	15.10	5.64	37.13	20.00	71.81	11.27	16.92
	Fallow	1.22	36.84	15.21	14.57	5.24	36.19	17.60	70.23	11.39	18.38
Clemson	Cotton	1.37	31.12	12.60	12.62	6.24	31.01	25.06	75.10	10.16	14.74
	Cotton-(vetch)	1.33	34.24	12.90	10.82	3.11	35.42	17.61	81.76	9.12	9.12
	Cotton, 8 T. manure	1.31	33.67	13.60	11.30	3.98	35.77	20.55	80.64	8.78	10.58
	Cotton-(vetch), 8 T. manure	1.32	34.28	13.01	11.05	4.83	35.60	24.07	79.95	8.82	11.23

* Date represent analyses of original soil.

cannot be directly correlated with run-off under field conditions, as the run-off may be influenced not only by soil conditions, but also by growing crops.

Other soil properties that are undoubtedly associated with erodibility of

soils are shown in table 5. The volume weight, saturation capacity, field moisture capacity, and moisture equivalent appeared to be directly related to one another and to the organic matter content. In all cases, volume weight definitely decreased when amounts of organic matter increased. There was not so much variation in the volume weight of the soil from the Greer experiment as from the other experiments, but this was attributed to the higher initial organic matter content of this soil. Bermuda grass sod produced the greatest effect on volume weight. The soil from the sod plat was capable of absorbing and retaining a higher percentage of moisture, as was shown by the water at saturation and the field moisture capacity, whereas the fallow plat had a higher volume weight and a relatively lower saturation capacity.

The percentage volume of macropores as shown for the various cropping systems indicated that soils well supplied with organic matter had the greatest effective porosity. Bayer (2) suggested that soil porosity plays an important role in water movement and that the micropores are important largely in storage. Erosion, under the field conditions represented in this experiment, appeared to be associated with the volume of the macropores, as all the soil-conserving rotations had a greater effective porosity and produced a marked retardation in soil and water losses in comparison with the soil-depleting rotations, which had a lower percentage of macropores and larger soil and water losses. The continuous sod plat did not show such a direct correlation. The plat had a higher percentage of macropores but also had an extremely low erosion loss. The erosion losses from soil on these plats, however, were undoubtedly complicated by the vegetative effects of sod.

Either the suspension percentage or the dispersion ratio as shown for soils under various cropping systems appears to be a fair single criterion for prediction of erosional behavior of soils. The general correlations for these two evaluations of erodibility are that low suspension percentages and low dispersion ratios are prevalent in soils which have had legume crops included in the rotation systems; whereas higher suspension percentages and dispersion ratios are found in soils after nonlegume rotations. The effects of additions of organic matter to a soil are very conclusively demonstrated by these data, and undoubtedly organic matter, either directly or indirectly, has an important influence on the ultimate structure of the soil.

SUMMARY

Studies on the effects of various cropping systems on the erodibility of soils are presented for plats at Tigerville, Duncan, and Greer. The data show that certain soil-conserving legume crops in a rotation not only reduced soil and water losses during the actual growing period of the legumes, but also made the soil less susceptible to erosion during the succeeding year when cultivated crops were grown.

A comparison of certain physical and chemical properties such as organic matter, humus, aggregation, volume weight, saturation capacity, field moisture

capacity, suspension percentage, dispersion ratio, percolation, and porosity were determined to note any correlation existing between erosion and soil properties affected by various cropping systems. The determinations of these soil properties under various cropping systems show considerable variations between soil-conserving rotations and soil-depleting rotations.

Organic matter content appears to be either directly or indirectly associated with the physical properties that are important in soil structure. Increases in the content of organic matter since the outset of the experiment resulted from rotations which included leguminous green manure crops, and decreases occurred in corn-cotton rotations, whereas the changes resulting from cropping systems were insignificant where the content of organic matter was abnormally high at the outset of the experiment.

Soil aggregation was influenced by the various erosion control crops. Bermuda grass sod increased the organic matter content, and as a result the soil under this type of cropping was in a high state of aggregation. The differences were most marked in the small sized aggregates, as indicated by the low percentage of <0.02 mm. aggregates, whereas a slight increase was noted in the >0.5 mm. aggregates. Vetch and lespedeza used in their respective rotations were not so effective as the Bermuda grass sod in promoting aggregation; however, a lower percentage of small aggregates was found on the lespedeza and vetch plats than on the corn-cotton rotations which did not include a legume.

Soils to which either green manure or barnyard manure was applied had lower volume weights, higher saturation capacities, and higher field moisture capacity than soils from soil-depleting rotations where only crop residues were added. This fact indicates a close correlation between these physical properties and organic matter.

Cropping practices also had an influence upon the dispersion ratio, suspension percentage, and porosity. Soil porosity, as indicated by the percentage volume of macropores, also appeared to be associated with erosion losses, as large soil and water losses usually occurred on soils with the lowest porosity, and smaller losses occurred on soils with higher porosity. The suspension percentage and the dispersion ratio showed significant correlations with erosional behavior of soils under field conditions and appeared to be good single indexes for predicting soil and water losses by laboratory methods.

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EFFECT OF CHLOROPICRIN FUMIGATION ON NITRIFICATION AND AMMONIFICATION IN SOIL¹

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Because of the interest that has developed in the use of volatile chemicals for partial soil sterilization The Rhode Island Agricultural Experiment Station has studied the use of chloropicrin (CCl_3NO_2). The primary objective in most experiments involving the use of this chemical for soil fumigation has been to control some specific, soil-harbored plant pathogene, little or no consideration being given to the effect which the treatment would have on the soil micro-organism population as a whole. Where pathogenic organisms were controlled, crop yields were greatly increased, as might be expected. In some experiments where disease was felt to be of minor importance, however, large increases in growth and yields were obtained. For example, yields of carrots and onions were increased about 50 per cent, and pepper, tomato, and eggplant yields were at least doubled. In many such instances, because of the lack of apparent disease, it was difficult to explain entirely these unexpected increased yields on the basis of controlling any specific pathogenic organism. This work was initiated, therefore, to determine what effect the soil treatment has upon the summation of the metabolic activities of the flora and fauna of the soil.

REVIEW OF THE LITERATURE

The relevant literature indicates that during the early part of the present century much work was done concerning the effect of so-called volatile antiseptics upon soil organisms and the effect of treatment on subsequent plant growth. It has been recognized that partial sterilization or treatment of the soil with heat or chemicals generally results in an increase in productivity of the soil. The vast amount of work done on this subject, however, has resulted in several conflicting statements and hypotheses. This confusion has undoubtedly arisen because of the fact that so many different factors are concerned with increasing plant growth. Variations would occur, for example, depending upon the agent used to sterilize the soil and upon the initial physical, chemical, and biotic condition of the soil treated.

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An excellent summary of early work on partial soil sterilization is presented by Kopeloff and Coleman (11). From this and more recent literature, it appears that the majority of the workers have ascribed the beneficial effects of partial sterilization to increased amounts of plant food, especially nitrogen, made available for plant use as a result of increased bacterial activity. Such workers as Russell and Hutchinson (13, 14), Hiltner and Störmer (9), Coleman (2), and Greig-Smith (6) seem to agree that increased bacterial activity is responsible, even though they may disagree as to just how this is brought about.

More recently Waksman and Starkey (18) have confirmed by experiment that partial sterilization results in an increase of the bacterial population and in ammonium-nitrogen accumulation. They explain this change as being due to a combination of factors; namely, changes in physical and chemical conditions of the soil, destruction of soil microorganisms thereby making their cell constituents available as a source of energy, changing the equilibrium of the microbiological flora, and the economical conversion of organic nitrogen to ammonium nitrogen.

Evidence has been reported in apparent opposition to the preceding concepts. Sinker (15) found that an equivalent amount of growth could not be obtained merely by the addition of large amounts of fertilizer. Gainey (4) demonstrated that increased yields could be obtained by treating the soil even though the numbers of bacteria were not increased. Also, Matthews (12) showed that chloropicrin treatment did not result in increasing the numbers of bacteria so much as did other antiseptics. Smith (16) in more recent work, however, has indicated that bacteria increased more rapidly in treated than in untreated soils.

Another explanation has been presented by Bolley (1) and others who believe that elimination of pathogenic fungi may have more to do with increase in crop growth than is ordinarily supposed. Jamieson (10) believes that the benefit is due to riddance in varying degrees of the forms of animal life in the soil that prey on plants. It has been generally recognized that the more unfavorable the initial biotic condition of the soil to plant development, the greater is the increase in subsequent productivity following treatment. Moreover, virtually all the workers have reported that an increase in yield could be expected wherever disease organisms were controlled by treatment.

Undoubtedly, the factors indicated by these workers were of major importance with regard to the particular soils or chemicals investigated. The status of chloropicrin, therefore, remains to be determined with regard to the effect which it has on the metabolism of the soil flora and fauna, the object being to determine whether there is an increase in bacterial activity which is of sufficient magnitude to increase the available nitrogen enough to account for some of the increases in growth recorded. Failure to find increasing bacterial activity would indicate the necessity of further investigations to ascertain whether or not beneficial effects are due to the destruction of some of the less evidently harmful organisms.

EXPERIMENTATION

In order to measure the comparative nitrogen conversion activities of the soil organisms in treated and untreated soil, a modification of the method recommended by Waksman (17) for determining the rate of ammonification and nitrification was used. It consisted essentially of determining at intervals the rate of nitrification of ammonium sulfate and the ammonification and nitrification of dried blood. Thus, the effect of fumigating the soil with various dosages of chloropicrin on the subsequent activities of the surviving micro-organisms during the growing season could be ascertained.

The soil used was Bridgehampton very fine sandy loam, taken from a field which had been cultivated for a number of years. This field had been fertilized with stable manure at the rate of 16 tons per acre the previous season, and it contained about 6.59 per cent organic matter. The H-ion concentration of a

TABLE 1

Dosages of chloropicrin used for fumigation and the forms and amounts of nitrogen added

TREATMENT	DOSAGE OF CHLOROPICRIN PER CUBIC FOOT	NITROGEN COMPOUND ADDED	AMOUNT OF NITROGEN ADDED
	cc.		p.p.m.
1	0	None	0
2	0	(NH ₄) ₂ SO ₄	300
3	1	(NH ₄) ₂ SO ₄	300
4	3	(NH ₄) ₂ SO ₄	300
5	9	(NH ₄) ₂ SO ₄	300
6	0	Dried blood	265
7	1	Dried blood	265
8	3	Dried blood	265
9	9	Dried blood	265

composite sample was pH 6.15. It had a water-holding capacity of 54 per cent on the dry soil basis.

Partial sterilization was carried out in glazed earthenware crocks. The jars were nearly filled with 18 pounds of screened soil. Pure chloropicrin was applied in a single hole that extended almost to the bottom of the vessel. The amounts of chloropicrin applied were equivalent to dosages of 1 cc., 3 cc., and 9 cc. per cubic foot of soil. At the time of treatment, the soil contained approximately 21 per cent moisture on a dry weight basis. Immediately after treatment the jars were sealed with glue-coated paper. Four days after treatment the soil was removed from the crocks and spread out to aerate.

Twelve days after treatment samples from each of the various treatments and from the untreated soil were placed in pint widemouthed glass jars. Each sample contained the equivalent of 100 gm. of dry soil. After the samples were placed in the jars, ammonium sulfate was added to some, and dried blood to others, making nine different treatments of 32 samples each (table 1).

To those jars receiving ammonium sulfate, 210 mgm. of calcium carbonate was added to neutralize the resultant acidity.

In order to establish the nitrogen level at the time of the addition of the fertilizer, samples of soil to which no nitrogen compounds had been added, but which had received the various chloropicrin treatments, were analyzed for nitrates, nitrites, and ammonium nitrogen. This also indicated the chemical changes that had taken place during the 12-day aeration period. It was found that the 1-cc. dosage had no effect on nitrification, but that the 3-cc. and 9-cc. treatments had inhibited nitrification during this period as compared with the untreated soil. The ammonium-nitrogen content was about the same in all cases.

After the addition of the fertilizer the water content of each of the soil samples was raised to approximately 60 per cent of its water-holding capacity. The uncovered jars were placed in an oven and incubated at 28°C. A fan was placed in the incubator to ensure circulation of air. The moisture content of the soil was maintained at 50 to 60 per cent of its water-holding capacity by regular replenishment of the water lost.

Analyses were made at intervals by removing four jars from each of the nine treatments. Half of these were analyzed for nitrates and nitrites, and the other half for ammonium nitrogen. In this way duplicate results were obtained for each treatment. The nitrates were determined by the phenol-disulfonic acid method (7), the nitrites by the sulfanilic acid-naphthylamine method (3), and the ammonium nitrogen by Harper's method (8). Since changes took place more rapidly in the earlier part of the experiment, the intervals between the determinations were shorter during that period.

RESULTS

The results obtained can best be presented in graphic form. The figures used in constructing the graphs were obtained by averaging results from duplicate samples.

In figure 1 note should be made that the untreated soil and the soil receiving 1 cc. chloropicrin per cubic foot had a nitrate-nitrogen content at the time of addition of the nitrogen compound of about 38 p.p.m.; whereas the soil treated with 3 cc. and 9 cc. contained about 18 p.p.m. of nitrate nitrogen. This was due to the fact that nitrification had taken place in the former case, from the time of treatment 12 days previous. In the soils receiving 3 cc. and 9 cc. of chloropicrin, however, nitrification had been inhibited during the period of aeration.

Further examination of figure 1 reveals that at the end of the 12-day period, nitrification was resumed in the 3-cc. treated soil. Moreover, the rate of nitrification was about parallel to that of the untreated and the 1-cc. treated soil. In the soil receiving 9 cc. chloropicrin, nitrification was inhibited for about 90 to 100 days. At that time either an unkilld residue of bacteria became active or the soil was reinoculated. Since retardation of nitrification

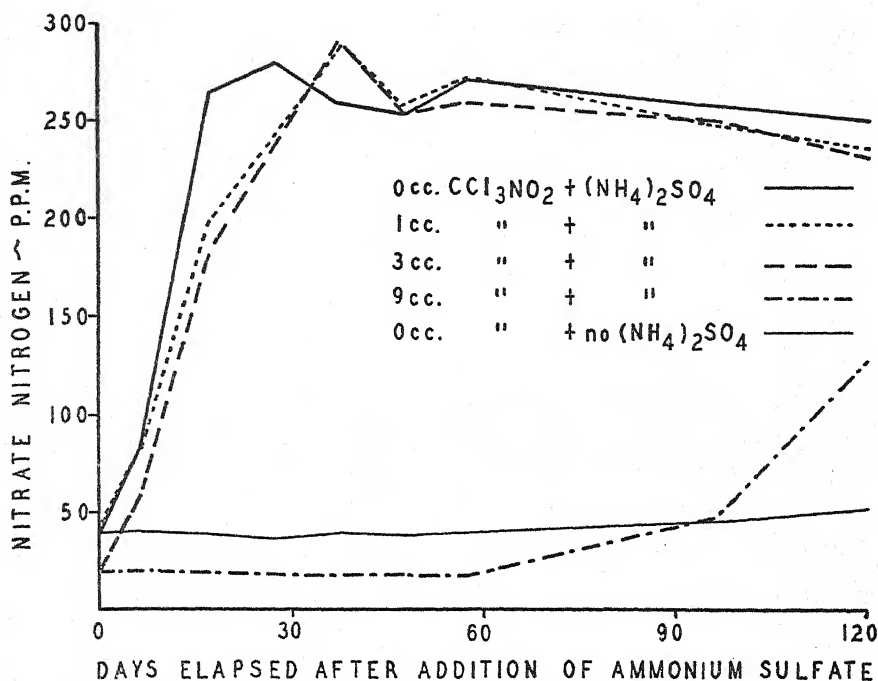


FIG. 1. EFFECT OF CHLOROPICRIN ON THE NITRIFICATION OF AMMONIUM SULFATE

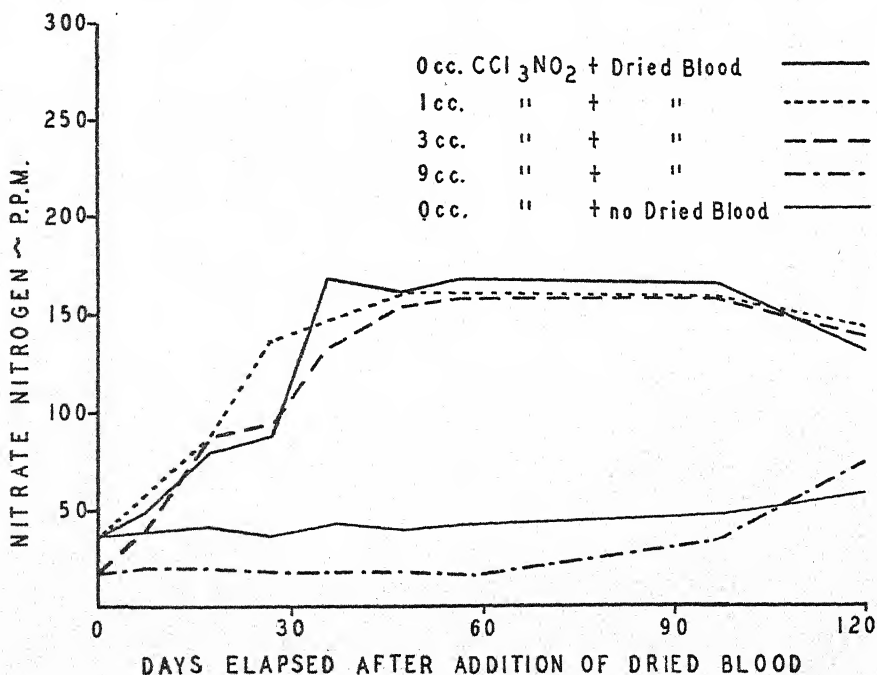


FIG. 2. EFFECT OF CHLOROPICRIN ON THE NITRIFICATION OF DRIED BLOOD

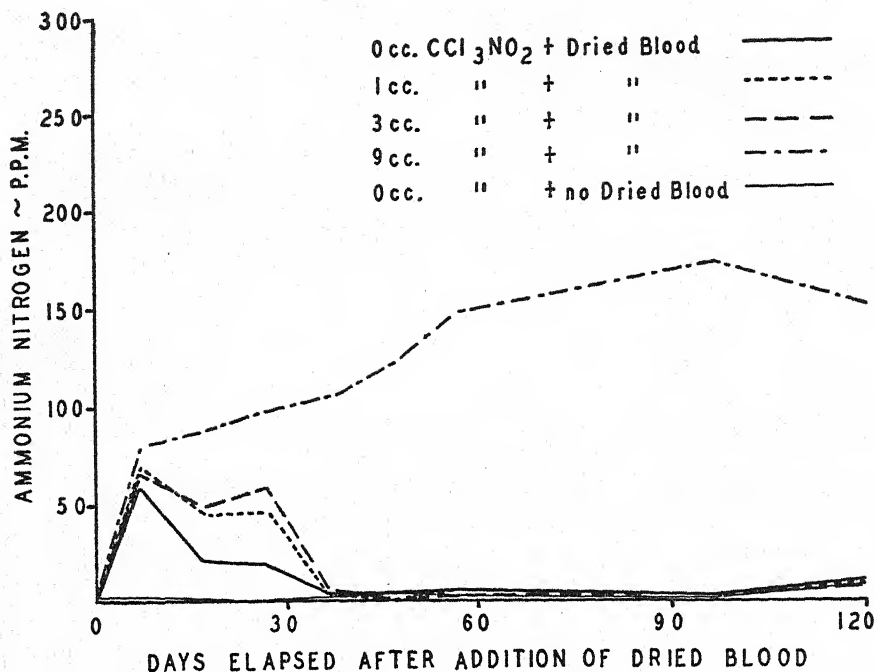


FIG. 3. EFFECT OF CHLOROPICRIN ON AMMONIUM-NITROGEN ACCUMULATION FROM DRIED BLOOD

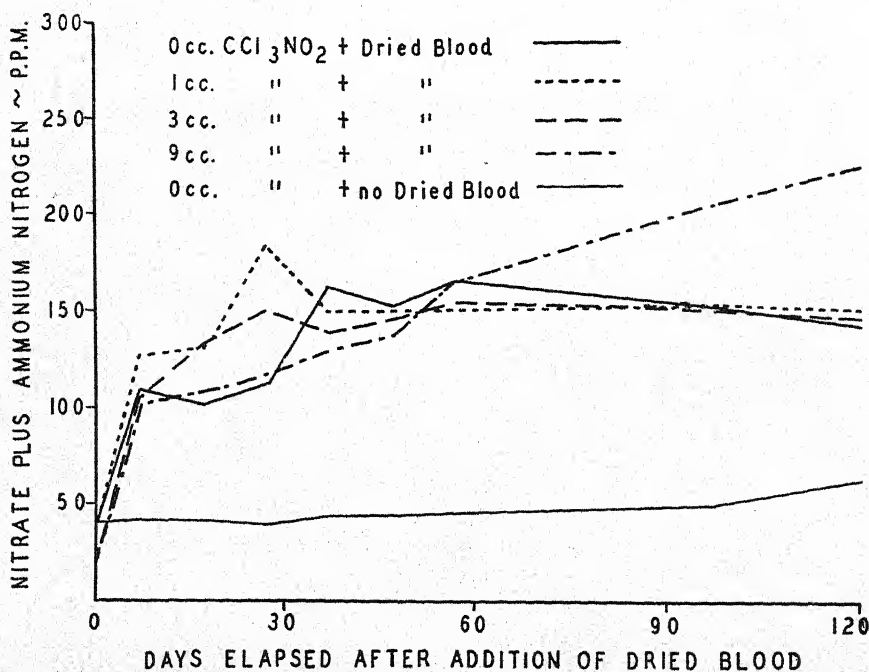


FIG. 4. EFFECT OF CHLOROPICRIN ON THE TOTAL ACCUMULATION OF NITRATES AND AMMONIUM NITROGEN FROM DRIED BLOOD

for a similar length of time was also observed in duplicate samples of the soils receiving the dried blood, it does not seem probable that nitrification was resumed because the soil had become reinfested. The rate of nitrification was slow even after the 90-day period. The resulting amount of nitrates, as well as the rate of nitrification in the 1-cc. and 3-cc. treated soils, was approximately the same as in the untreated soil. As ammonium-nitrogen determination on similarly treated soils revealed identical results, the graph showing the residual ammonium nitrogen has been omitted.

Figure 2 reveals that the amount of nitrates oxidized from the dried blood was about the same in the untreated and the 1-cc. and 3-cc. treated soils. In the soil receiving the 9-cc. treatment, nitrification was again inhibited. In figure 3 it may be seen that the 9-cc. treatment did not inhibit ammonification, but appears to have stimulated it slightly. Since this treatment inhibited nitrification, however, this graph shows an accumulation of ammonium nitrogen. In the untreated and in the 1-cc. and 3-cc. treated soils where nitrification was not seriously inhibited, ammonium nitrogen did not accumulate because it was immediately converted into nitrates.

In order to ascertain whether or not any of the treatments increased the total amount of nitrogen made available for plant use, the ammonium and nitrate nitrogen produced from the dried blood were added together. The results, as shown in figure 4, indicate that the soils receiving the 1-cc. and 3-cc. treatments produced no more available nitrogen than did the untreated soil. In the 9-cc. treated soil, however, there was a material increase in available nitrogen after 60 days. This increase produced by a high dosage is probably due to increasing the ammonifying power of the soil, but the effects appeared late in the experiment.

The nitrite-nitrogen determinations revealed that in no case did nitrites accumulate. The greatest amounts were found during the period when large amounts of ammonium nitrogen were being converted to nitrates. Even then, however, the nitrites amounted to only 2 to 3 p.p.m. Other than at this period, the nitrite-nitrogen content was negligible, being less than 1 p.p.m.

DISCUSSION

The results indicate that in many respects chloropicrin behaves similarly to other so-called volatile antiseptics which have been tried for soil fumigation. Inhibition of nitrification has been reported by many workers who have used such substances as carbon disulfide and toluene. Chloropicrin is no exception to this, and it appears that increasing the dosage tends to increase the interval of time before active nitrification is resumed. Ammonification is not retarded, probably because many of the ammonifying bacteria are spore-formers and are thus difficult to kill. When nitrification is inhibited, ammonium nitrogen accumulates. Smith (16) in recent work confirms these results by finding that chloropicrin killed the nitrifying bacteria readily, whereas it had little effect upon the spore-forming bacteria. He obtained retardation of nitrification at

lower dosages of chloropicrin than are reported here, probably because the treatment was performed under more nearly optimum conditions.

Care should be taken not to assume that the results obtained under laboratory conditions will necessarily be duplicated under field conditions. The exact relationship is difficult to ascertain. In the laboratory the soil conditions can be easily controlled, and, more important, the fumigant can be confined for longer periods. The field dosage that resulted in increased yields was 2 cc. placed in holes 15 inches apart; less than the 3-cc. treatment used in this experiment. From other comparative tests with specific organisms under laboratory and field conditions, it does not seem probable that the field dosage mentioned would be sufficient to inhibit nitrification for any great length of time. Assuming that there was a retardation of nitrification in the field, the question arises as to what effect the resulting ammonium-nitrogen accumulation would have on plant growth. It does not seem probable, however, that the advantages of having nitrogen in the form of ammonium nitrogen instead of as nitrates could be of sufficient value to account for the increase in crop yields.

The outstanding difference between these results with chloropicrin and those obtained by investigators working with other chemicals, is the fact that neither the rate of nitrification nor the total amount of nitrogen made available was markedly increased over that in untreated soil. It is difficult to detect increased activity in treated over untreated soils when the rate of nitrification in the untreated soil is so rapid. The soil used in this experiment, however, was essentially the same as that which had responded well to chloropicrin fumigation, as reflected by increased crop yields. Because of the results obtained in this experiment, therefore, it does not seem probable that the increase in available nitrogen was responsible for the increase in yields obtained.

Assuming that increase in available nitrogen is not always the deciding factor in increasing crop yields, it seems advisable to turn toward another and more feasible explanation. It should be recalled, first, that the soils fumigated had been cropped for a number of years; second, that in plats where the greatest increases in yields were obtained, the same crop had been grown the previous year. Most workers, as indicated in the review of the literature, have reported that wherever disease organisms are controlled, increase in yields may be expected. Further, it has often been suggested that in virtually all soils that have been in use for a number of years, particularly for growing the same crop, there is an accumulation of undesirable organisms. The exact injury done to plant roots by these organisms, particularly fungi, is difficult to ascertain and is not generally given sufficient prominence. Since Smith (16), Godfrey (5), and others have shown chloropicrin to be a powerful lethal agent, particularly against fungi, it seems likely that the benefits of chloropicrin soil fumigation are in a large part due to the control of undesirable organisms, especially fungi.

It is probable, therefore, that plants grown in fumigated soil develop extensive, fibrous, uninjured root systems because they are subjected to fewer inhibitory organisms. This is reflected in vigorous growth and increased yield.

SUMMARY

The effect of fumigating soil with chloropicrin upon the subsequent rate of ammonification and nitrification was studied.

Low dosages of chloropicrin were found to have little effect on nitrate formation; but, as the dosage was increased, nitrification was inhibited. The length of the inhibition period was dependent on the dosage of chloropicrin.

In no case was ammonification inhibited; therefore, in some instances the inhibition of nitrification resulted in an accumulation of ammonium nitrogen.

The total amount of nitrogen made available for plant growth was not materially increased except where high dosages of chloropicrin were used.

In view of the data obtained from this experiment the increases in plant growth obtained by treating the soil with low dosages of chloropicrin cannot be accounted for solely by the hypothesis that more nitrogen was made available for plant growth.

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THE INFLUENCE OF THE DEGREE OF SATURATION OF SOIL COLLOIDS ON THE NUTRIENT INTAKE BY ROOTS

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In order to elucidate mineral nutrition of plants in soils, plant physiologists have developed the method of artificial culture solutions of known compositions. For almost a century this method proved most fruitful, and it has furnished the fundamental principles of present-day knowledge of mineral nutrition of plants. With the advance of the study of colloidal phenomena in soils, especially with regard to the role of colloids in influencing the composition of the soil solution, it became apparent that the artificial nutrient solution medium was an inadequate basis for interpretation of the actual growth conditions existing in many soils. Here the simple system "root/solution" is complicated by the presence of colloidal clay particles which compete with the plant root for certain nutrient elements. Consequently, in recent years the study of absorption of nutrients by plants in the presence of colloidal suspensions of known compositions has come into prominence (1).

STATEMENT OF PROBLEM

Nutrient ions which are adsorbed on the surfaces of clay particles are a part of the diffuse electrical double layer and cannot be accumulated by plants unless first displaced from the sphere of attraction of the clay micelle. Several types of mechanisms may be operative in the process of liberation of cations adsorbed on clay particles. In the special case of K-clay, for example, release of potassium may be brought about by:

Hydrolysis. The H ions of water replace the adsorbed K ions.

Acid exchange. H ions from acids dissolved in the soil solution, particularly carbonic acid and nitric acid, exchange K ions from the surface of clay particles.

Salt exchange. Many soils of arid regions contain considerable amounts of inorganic salts (CaCl_2 , Na_2SO_4) which participate in exchange reactions.

According to the soil solution theories of plant growth in soils, ionic exchange between soil solution and clay surfaces is a prerequisite for the intake of adsorbed ions by plants. In other words, the mechanism of nutrient absorption by roots in colloidal suspensions involves—in contrast to solutions—not

¹ Division of Plant Nutrition, College of Agriculture, Berkeley, California. The experimental data have been taken from Dr. Ayers' thesis: "The intake of potassium by excised barley roots from solutions and colloidal clay suspensions."

one step but two steps. In true solutions, as soon as an ion or ion-pair strikes the root surface, it is ready for intake, whereas in colloidal solutions this step must be preceded by the release of the ion from the surface of the clay particle. As a general rule, the plant itself provides the necessary replacing agents. It may be aided in considerable part by the action of microorganisms.

The present study deals with a comparison of the intake of potassium from colloidal clay systems and from true electrolyte solutions. Special emphasis is placed on the influence of the degree of saturation of colloids because this is one of the major factors governing the availability of adsorbed ions in soils. No effort is made to evaluate the contact exchange theory of Jenny and Overstreet (9), which provides an additional mechanism of plant nutrition in soils.

The presentation of the data embraces the following parts:

Theoretical and experimental study of ionic exchange as dependent on the degree of saturation, with special reference to the exchange with carbonic acid.

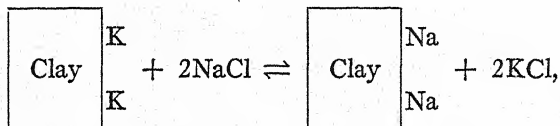
Accumulation of adsorbed K from clay suspensions by barley roots.

Accumulation of K from salt solutions which contain identical amounts and proportions of total K as the colloidal solutions.

On the basis of these comparable sets of data, it should be possible to elucidate quantitatively the differences in nutrient-supplying power of solutions and suspensions.

ION EXCHANGE AND DEGREE OF SATURATION

Simple exchange reactions of the type,



may be expressed quantitatively by thermodynamic (15) or kinetic equations (7). In natural soils, pure clay systems (e.g., K-clay, Na-clay, etc.) are rarely found. The colloidal clay particles almost always carry a variety of cations.

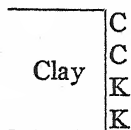
If a specific cation, say potassium, is singled out, the remaining adsorbed cations (Na, Ca, H, etc.) may be designated as *complementary* ions. The relationship between K and the complementary cations is known as *degree of saturation*, which is usually expressed on a percentage basis. The degree of K saturation is defined as

$$\frac{K}{K + C} \times 100,$$

where *C* denotes the amount of the exchangeable, complementary cations, and the sum (*K* + *C*) corresponds to the saturation capacity of all colloidal particles present in the system.

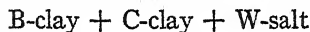
From the viewpoint of mineral uptake by plants in soils, the degree of saturation assumes a dominant role because it controls the exchangeability, and

therefore the availability, of nutrient ions. Let us, for example, consider the following type of cation coating of a clay particle:

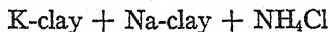


If we place the particle in a solution which contains a third cation, say NH_4 , the amount of K replaced depends on the number of complementary cations present on the surface, in other words, on the degree of K saturation. Moreover, the kind of complementary ions also is of importance. If these ions are held loosely, they will tend to depress further the outgo of potassium. Evidently the replacement of adsorbed K in a multiple-ion system is governed by rather complicated interactions of adsorbed and released cations.

It will be instructive to isolate the role of the degree of saturation and the nature of the complementary cation for a relatively simple system. Let us assume that a colloidal particle contains exchangeable cations of the type "B" (corresponding to the special case of potassium) and complementary cations "C." To this system we add a solution containing ions of the type "W" in amounts equal to the number of "B" ions in the system (symmetry concentration). In general such systems may be prepared by mixing the following substances:



A special case may be represented by the following example:



The essential problem with which we are dealing is this: How many B ions will be replaced by W ions if the amount and kind of the complementary C ions vary within wide limits?

A mathematical expression which answers the foregoing questions may be derived according to reasoning previously developed (7) for an idealized ionic exchange model. The equation has the form:

$$b^2 \left(2 \frac{V_c}{V_b} - 2 \right) + bb_0 \left[\frac{V_c}{V_b} \left(\frac{1 - 2D}{D} \right) + 3 \right] - b_0^2 = 0 \quad (A)$$

The symbols have the following meaning: b_0 = number of B ions initially adsorbed, b = number of B ions replaced, D = degree of saturation of B ions (divided by 100), V_b = oscillation volume of B ions (taken to be equal to V_w , the oscillation volume of W ions), V_c = oscillation volume of C ions.

It will be noted that the equation contains the two required variables D , degree of saturation, and V_c , the adsorbability of the complementary ion. Three typical, calculated curves are given in figure 1. They reveal several striking features.

First, the curves clearly show that a decreasing degree of saturation reduces

the amount of B ions replaced by W ions. For the specific case in question, the W ions will replace 50 per cent of the B ions, if no C ions are present (degree of saturation of B is 100 per cent). The replacement of B approaches zero when the proportion of C ions to B ions on the colloid becomes very large.

In the second place, the influence of the nature of the complementary ion is highly significant. Three characteristic cases are illustrated in figure 1. If the C ions are held by the particle more tightly than are the B ions, the replacing W ions favor the B ions and the degree of saturation has little effect as long as it does not fall below 25 per cent (upper curve). If, on the other

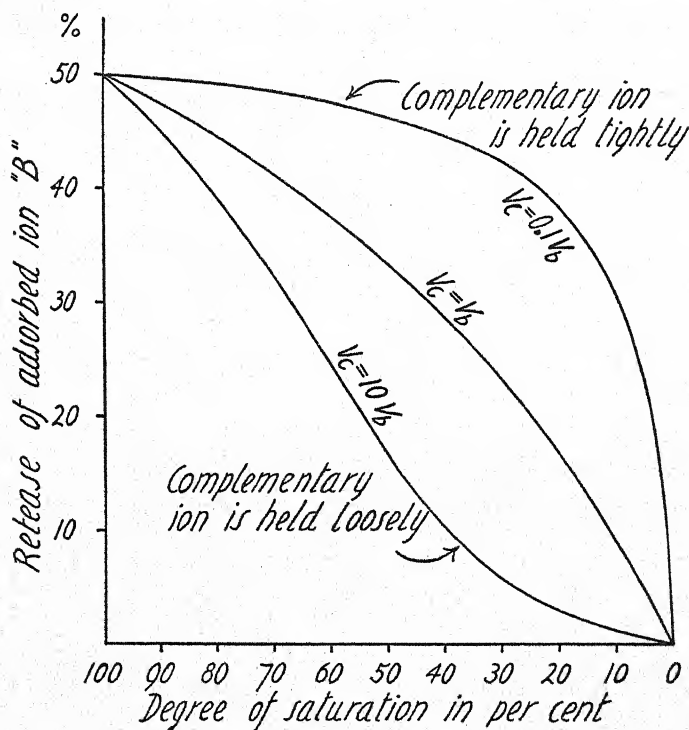


FIG. 1. THEORETICAL EXCHANGE CURVES, SHOWING THE INFLUENCE OF DEGREE OF SATURATION AND NATURE OF COMPLEMENTARY ION

hand, the complementary ion is held loosely, as compared with B, the replacing agents will exchange C rather than B and the role of the degree of saturation assumes formidable proportions (lower curve). If all ions possess equal oscillation volumes, that is, equal adsorbability, a relationship results which is indicated by the middle curve. The arbitrarily selected ratios (10:1) of the oscillation volumes are conservative. In the case of adsorbed Na and H the shape of the curves would be highly exaggerated, since $V_{Na} : V_H$ has a value of 200 [compare (7)]. Vageler (14) also has developed an equation which describes base exchange as a function of the degree of saturation. It is essentially of

empirical nature and does not stress the significance of the properties of the complementary ions.

An experimental illustration of the foregoing theoretical discussions is presented in figure 2. It refers to K-clay systems to which were added various amounts of Ca-clay, or Na-clay, or NH_4 -clay. The exchanging electrolyte was HCl. The concentrations of K (as K-clay) and of HCl were 1 m.e. per liter. Although the type of ions does not quite conform to the assumptions postulated in the equation (especially $V_K \neq V_H$), the general relationships are

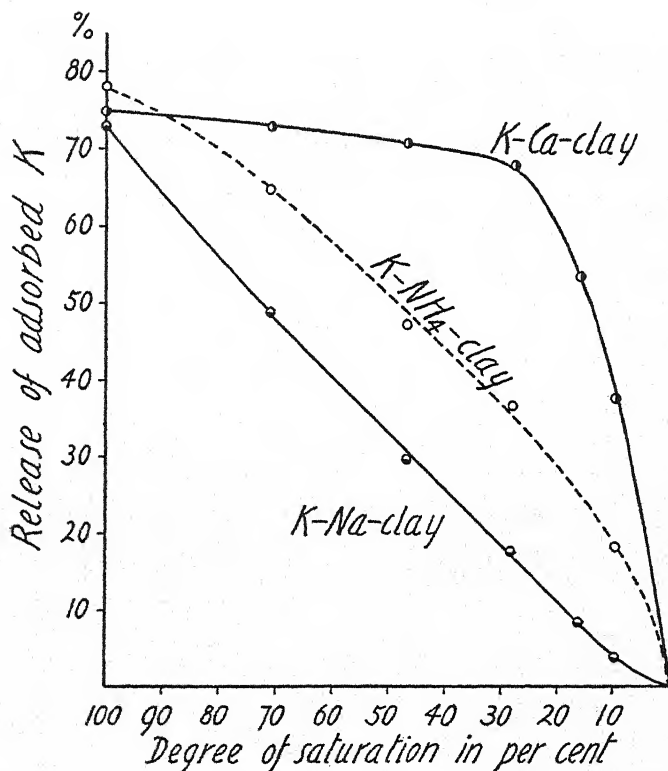


FIG. 2. EXCHANGEABILITY OF ADSORBED K AS INFLUENCED BY DEGREE OF SATURATION AND NATURE OF COMPLEMENTARY ION. EXCHANGING AGENT: HCl

nevertheless clearly indicated. The adsorbability of the complementary ions decreases from Ca to NH_4 to Na, and the shapes of the curves are correspondingly manifested.

SOME BIOLOGICAL CONSIDERATIONS

Although theory and experiment demonstrate that the release of adsorbed ions decreases with lowering of the degree of saturation, it does not necessarily follow that the intake of adsorbed potassium by roots follows the same trend, for plants possess an inherent ability for pronounced selective absorption of

solution ions. The following considerations may throw some light on the relationships to be expected.

The experiments just cited show how much K is exchanged by a given amount of H ions under a given set of conditions. One might reverse the problem and ask the question: How high an amount of electrolyte must be added to systems of various degrees of saturation in order to exchange a constant percentage of the adsorbed potassium? For ions which are equally well adsorbed ($V_b = V_c = V_w$) the following relationship is obtained between B

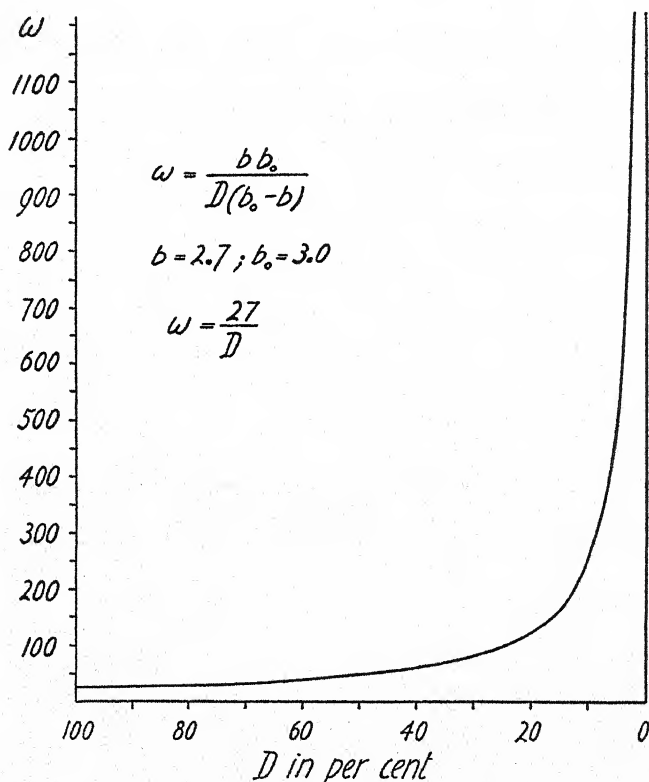


FIG. 3. AMOUNT OF ELECTROLYTE (w) NECESSARY TO REPLACE 90 PER CENT OF ADSORBED K AT VARIOUS DEGREES OF SATURATION (D)

ions initially adsorbed (b_0), B ions exchanged (b), W ions added (w), and degree of saturation (D):

$$b = \frac{b_0 w D}{b_0 + w D} \quad (B)$$

As will be shown presently, 100 gm. of excised barley roots are able to accumulate within 10 hours about 90 per cent of the adsorbed potassium from a 100 per cent saturated K-clay containing 3 m.e. of K in 3 liters of suspension.

With the aid of the preceding equation, figure 3 has been constructed. This indicates the amount of W ions necessary to replace 90 per cent of K (B ions) at various degrees of saturation. The phenomenal rise in the concentration of W ions at low degrees of saturation is impressive. At 100 per cent of saturation 27 m.e. of W will set free the 2.7 m.e. of K mentioned above. At 1 per cent of saturation the corresponding value is 2,700 m.e. of W. Now, the aforementioned barley roots produce only 32 m.e. of carbonic acid (5) during the period of experimentation (10 hours) and this represents the maximum amount of W available for the exchange reaction. It is far short of the amount necessary to replace 2.7 m.e. K at low degrees of saturation, even if we grant that H ions are somewhat better replacing agents than the W ions of equation B.

It should not be forgotten, however, that equation B neglects the selective accumulation capacity of the roots. It is an equilibrium equation, based on the assumption that nothing has been removed from the system. During the exchange reaction the roots constantly remove replaced K and shift the equilibrium in favor of K liberation. If we designate by r the fraction of exchanged K (or B ions) removed by the roots, the following equation is obtained:

$$rb^2 - b \left[b_0 \left(\frac{1-r}{D} + r \right) + w \right] + b_0 w = 0 \quad (C)$$

Figure 4, which is corollary to figure 3, graphically illustrates several specific solutions of equation C. The x-axis contains a selected range of degrees of saturation (3 to 25 per cent). On the y-axis are plotted the amounts of replacing W ions (w) which are necessary to exchange 2.7 m.e. K. The four curves relate to various values of r , that is, the fraction of exchanged K removed from the solution by the actively accumulating plant roots.

The uppermost curve refers to $r = 0$ and is merely a part of the curve of figure 3. The curve second from the top reflects the conditions when the roots remove 25 per cent of the K replaced. Compared with the status of no removal (uppermost curve), the values of w are consistently lower, especially at the lower degrees of saturation. At $D = 3.0$ per cent, only 675 m.e. W are necessary to replace 2.7 m.e. K, instead of 900 m.e. as is the case for $r = 0$. This tendency becomes the more pronounced the greater is the amount of K removed. When 75 per cent K is consumed by the roots, the corresponding value of w is only 227 m.e. If K is removed as fast as it is released from the clay particles, the equation yields a value of 2.7 m.e. w , which represents the minimum amount of any electrolyte necessary for replacing 2.7 m.e. K. Contact exchange (9) is the only mechanism which provides so efficient a removal of ions.

Evidently, the 32 m.e. CO_2 produced by the roots may or may not be sufficient to replace 2.7 m.e. K at lower degrees of saturation. It all depends on how efficiently the plants remove the exchanged K, a point emphasized by Hoagland (4) and by Truog (12). If the rate of intake is very high and if

this is an inherent property of the plant, then the degree of saturation would have no effect on the K absorption of the roots. On the other hand, if the accumulation rate is conditioned by the K concentration and the cation ratios of the solution, the degree of saturation should play a role in the nutrition of the plant. At low degrees of saturation, the bulk of carbonic acid functioning in exchange will be consumed in the release of complementary ions (C) rather than K ions, and the K concentration in the intermicellar liquid may become

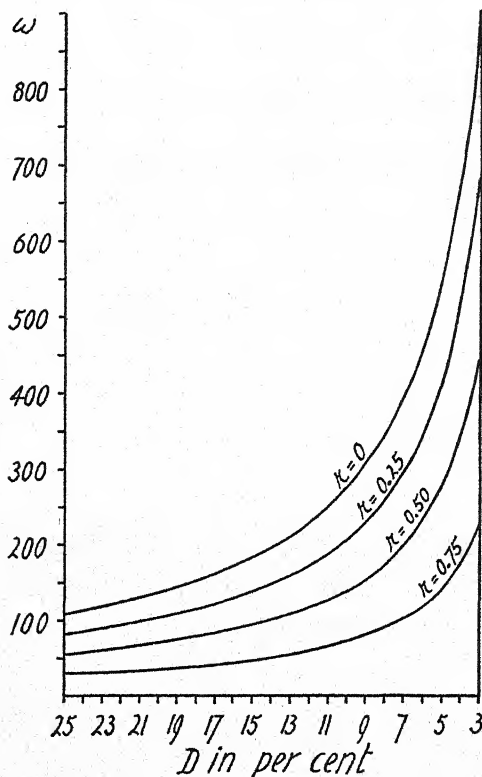


FIG. 4. EFFECT OF REMOVAL OF EXCHANGE K BY ROOTS (r) ON THE AMOUNT OF ELECTROLYTE (w) NECESSARY TO REPLACE 2.7 M.E. K AT VARIOUS DEGREES OF SATURATION (D)

so low and the C : K ratio so high as to overbalance the selective absorption tendencies of the roots.

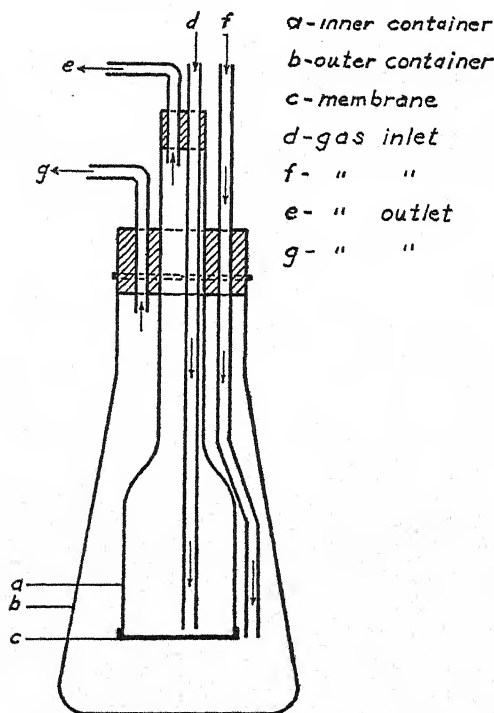
EXPERIMENTAL TECHNIC

Clay particles having an effective settling diameter of less than 0.2μ were separated from Yolo clay loam with the aid of Sharples supercentrifuge. Pure basic clays were prepared by leaching the colloids with salt solutions or by electrodialysis with subsequent addition of hydroxides. The base-exchange capacity of the clays varied from 59 to 67 m.e. per 100 gm. dry material.

All experiments were conducted with excised barley roots which were grown

and treated according to the method of Hoagland and Broyer (5). The roots had a high accumulation capacity for K. Approximately 100 gm. of fresh roots (about 8 gm. oven-dry) were immersed in 3 liters of the desired solutions and suspensions, which were continuously aerated. Accumulation of K was measured by analysis of the roots (3).

Special studies were undertaken to ascertain the influence of the K concentration and the time period on the accumulation of K by the roots. Both for K-clay and KCl an absorption maximum was reached at a total K concentra-



Exchange Flask

FIG. 5. EXCHANGE FLASK FOR THE DETERMINATION OF CO₂ EXCHANGE

tion of about 10 m.e. in 3 liters (10-hour periods). In all cases the roots accumulated more K from KCl than from K-clay. The time function was determined with systems containing 15 m.e. K in 3 liters. A maximum of intake was observed after 16 hours. Again the KCl solution proved to be the superior medium for K accumulation. In accordance with these findings the K level of all media was kept at about 1 m.e. total K per liter. The absorption time was restricted to 10 hours.

For the study of replacement of K from the clay suspensions by carbonic acid, a special "exchange flask" (fig. 5) was constructed which consisted of two

compartments, separated by a cellophane membrane. Clay suspension was placed in the inner container, distilled water in the outer. Carbonic acid was bubbled continuously through both compartments for 10 days. The amount of potassium found in the outer compartment was considered equal to the K concentration of the intermicellar liquid of the entire system.²

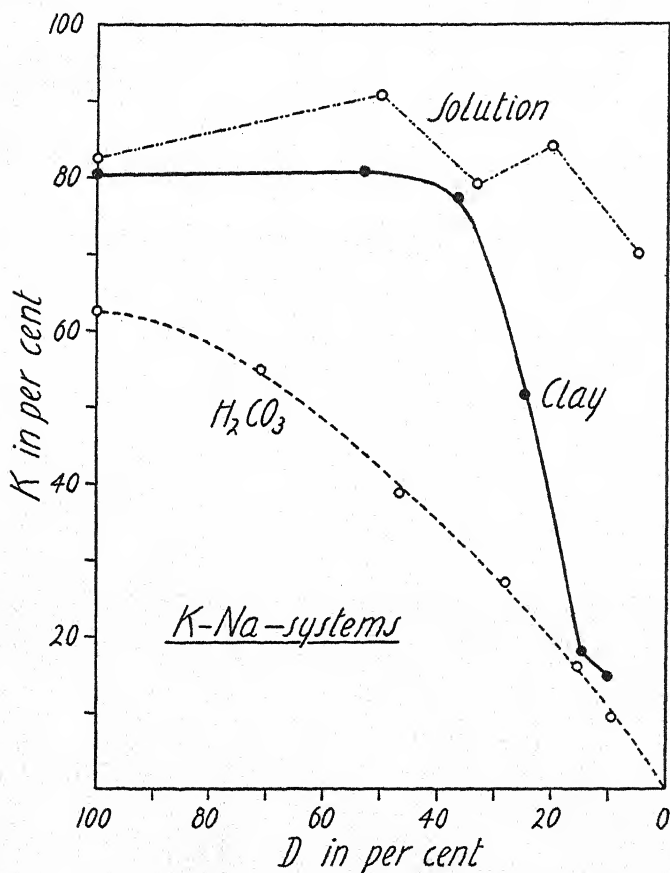


FIG. 6. ACCUMULATION OF K BY ROOTS FROM K-Na-SYSTEMS

EXPERIMENTAL RESULTS

Inasmuch as all experiments were comparable with regard to amounts and concentrations of K, type of roots, and absorption periods, it was possible to plot the results of corresponding series on one single graph. Each of the figures contains three curves, two of which express the K intake by roots from clay suspensions and salt solutions, and the third indicates the replacement by carbonic acid.

² The absolute amounts may be in error because of Donnan equilibria.

Potassium-sodium systems (fig. 6). From the chemical exchange curve it is evident that a saturated solution of carbonic acid replaces 62.5 per cent K from a pure K-clay (1 m.e. K per liter). With increasing amounts of Na-clay present in the system, the degree of saturation becomes lower, and the percentage of K replaced is correspondingly reduced. At very low degrees of saturation, less than 10 per cent of the total exchangeable K appears in the intermicellar liquid. The solid-line curve depicts the intake of K by excised barley roots from the K-Na-clay suspensions. Approximately 80 per cent K is taken up from the pure K-clay. The rate of change is relatively small as long as the degree of saturation does not drop below 40 per cent. As soon as the proportion of sodium to potassium on the clay becomes high, the intake of K amounts to only 15 per cent of the total K present in the suspension. No such drastic reduction is observed for the neutral salt solutions (dotted line). From pure KCl the roots accumulated 2.48 m.e., or 82.7 per cent. This value was relatively little affected by additions of NaCl, even to the extent of 57 m.e.

TABLE 1
K-Ca-systems

DEGREE OF SATURATION	CO ₂ EXCHANGE	ACCUMULATION OF K FROM	
		K-Ca-clay	KCl + CaCl ₂
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
100.0	56.6	80.5	82.6
30.0	55.5
25.0	52.5	89.5
20.0	48.0	77.6
14.6	40.0	68.2
10.5	31.0	50.0
10.0	30.0	101.1
5.0	16.0	91.5

in 3 liters solution. The initial pH values varied from 7.35 to 7.50 for the clays and from 5.60 to 5.70 for the salt solutions. At the end of the experiments the pH of the suspensions dropped to the range of 4.60 to 6.04; the solutions had values from 4.70 to 4.80.

Comparison of the three curves conclusively shows that the lack of K accumulation at low degrees of saturation is a consequence of the ion-exchange principles involved in the liberation of the adsorbed K.

Potassium-calcium systems (table 1). Substituting Ca in place of Na yields a new series of exchange and accumulation curves. First, the replacement of K by H₂CO₃ is scarcely affected by the presence of Ca as long as the degree of K saturation remains above 30 per cent. Unlike Na, Ca is held very tightly on the surface of the clay particles, and consequently, the H ions of carbonic acid readily exchange K ions. The same trend is observed for the accumulation curve. Although the analytical data scatter considerably, the total uptake of K remains relatively high at all degrees of saturation investigated.

At 10 per cent potassium saturation, the roots still obtained 50 per cent of all K present, whereas for the K-Na-clay the corresponding value was only 14.8 per cent. The K accumulation from chloride solutions appeared to be stimulated by the addition of CaCl_2 . This again points to the fact that any retardation in absorption of K by roots is related to the exchangeability of K on the clay particles. The initial reaction was 6.90 to 7.00 for the clays and

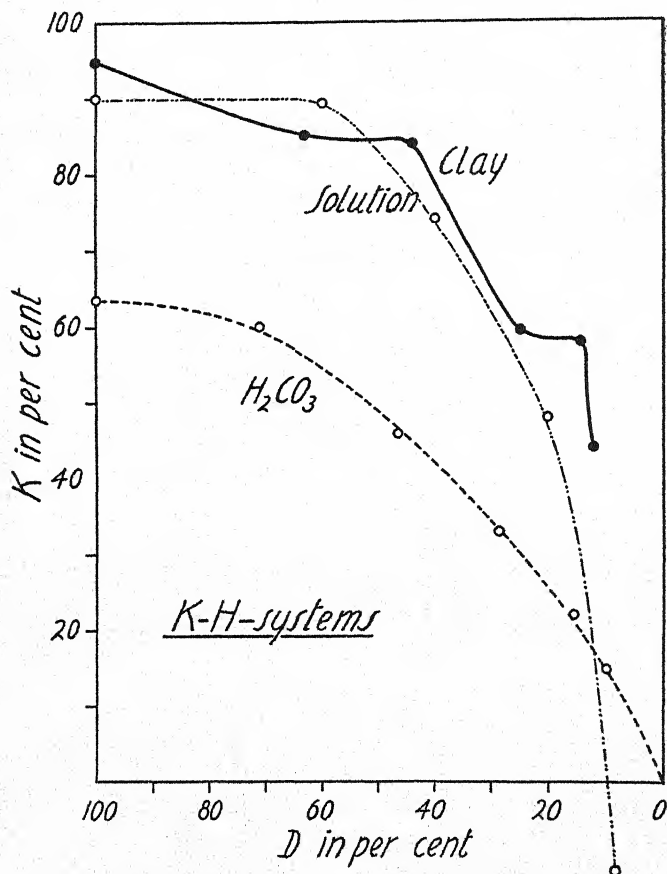


FIG. 7. ACCUMULATION OF K BY ROOTS FROM K-H-SYSTEMS

5.65 to 5.80 for the chloride solutions. The final pH values were 4.45 to 6.20 for the clays and 5.40 to 6.50 for the solutions.

Potassium-hydrogen systems (fig. 7). The presence of H ions on the clay particle brings about a gradual lowering of the exchange of K by carbonic acid. The K accumulation curve for the roots falls off in like manner. The same is true for the intake from solutions consisting of mixtures of KCl and HCl. Hydrochloric acid was injurious to the roots, as evidenced by their loss in turgor and of K ions.

It should be pointed out emphatically that the above KCl-HCl solution series gives a distorted picture of the influence of acid clays on K absorption. The pH values of the mixtures having high ratios of HCl to KCl were less than 2, whereas the corresponding clay systems were so strongly buffered that the final pH values of all suspensions fluctuated only from 4.20 to 4.35 irrespective of the degree of saturation. Hoagland and Broyer³ have shown that the

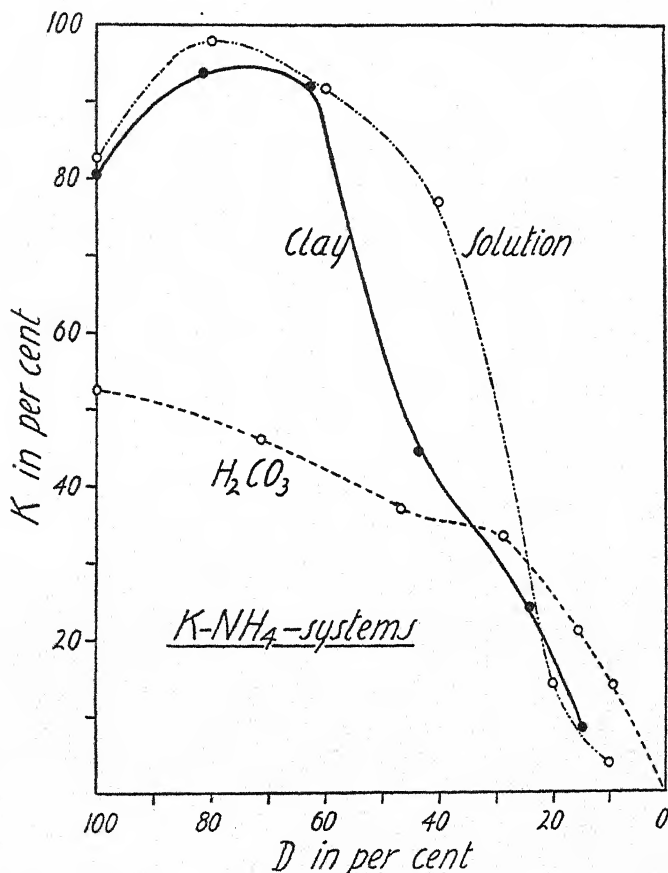


FIG. 8. ACCUMULATION OF K BY ROOTS FROM K-NH₄-SYSTEMS

intake of K by excised barley roots from solutions is relatively little affected within the pH range of 4.5-8.0. In harmony with these findings no injurious effect of the acid clays on the roots could be detected. We are thus led to the conclusion that the diminishing intake of K with lowering of the degree of saturation is conditioned by the reduced availability of potassium rather than by an injurious effect of hydrogen ions.

Potassium-ammonium systems (fig. 8). Small amounts of NH₄ ions on the

³ Hoagland, D. R., and Broyer, T. C. Unpublished data.

colloidal particles seem to stimulate the intake of K by the roots, but as soon as the degree of saturation falls below 60 per cent, the absorption of K reaches a very low level. At 14 per cent saturation, the roots recover only 8.4 per cent of K as compared with 18 per cent for K-Na-clay, 58 per cent for K-H-clay, or 68 per cent for K-Ca-clay. This sharp decline of K consumption from K-NH₄-clay, however, is not only a consequence of exchangeability but is also conditioned by physiological processes of the roots, since in the mixtures of KCl and NH₄Cl the roots behave in a very similar manner. In place of K the roots gained considerable amounts of nitrogen, which might have impaired the absorptive capacity for potassium. The pH values were of the same order of magnitude as those of the other salt systems.

DISCUSSION⁴

Probably one of the first investigators to study the effect of the degree of saturation on plant growth was Stohmann (10). He treated acid peat with extracts of barnyard manure and then leached the material for 3 weeks with large amounts of water. In this manner he obtained peat which had virtually all of the nutrient ions in the adsorbed state. This basic peat was mixed with various amounts of acid peat and planted to corn. The weight of the mature plants, in grams, was as follows:

<i>Growth Medium</i>	<i>Yield</i>
100 per cent degree of saturation.....	836
50 per cent degree of saturation.....	386
25 per cent degree of saturation.....	252
Acid peat alone.....	17.5

About 10 years ago, Gehring (2) showed for a series of German soils that the degree of saturation of K in soils tends to be related to the Neubauer test and to field response for K fertilization. The lower the degree of K saturation, the greater was the yield increase brought about by application of potash fertilizers. Soils which vary widely in total amount of exchangeable K, or soils which possess a high fixing power for K, however, would not be expected to follow this simple relationship.

With the development of colloid chemical methods and theories, it was possible to approach the subject under more rigidly controlled conditions. Jenny and Cowan (8) found that the yields of soybean plants grown in Ca-H-clay suspensions sharply decreased when the degree of saturation fell below 30 per cent. Albrecht and his students (1) extended these studies to other types of cations and to microscopic organisms. In particular, Horner (6) pointed out the significance of the nature of the complementary cation.

⁴Note during publication. The translation from the Russian of an important paper by S. S. Yarussov "On the availability of soil exchangeable cations for plants," in *Pedology* 1938: 799-828, was received too late for inclusion in the discussion. Yarussov's and our viewpoints agree in essential parts.

Tyner (13), using Prianischnikov's isolation method, observed a depressing effect of half saturated K-bentonites on the growth of various plant species.

There appears to be general agreement regarding the factual data on the relationship between plant growth and degree of saturation, but as to explanations, the opinions are divided. The present study convincingly shows, both by experiment and by theory, that the replaceability of a cation from a clay particle is depressed by the presence of complementary ions. This impedance in release of ions is reflected in the accumulation by plant roots. In some cases, as with K-Na-clays, the exchange principle appears to be the sole factor which limits the amount of uptake of K by excised barley roots; in others, especially for K-NH₄-clays, some antagonistic or competitive effect of the complementary ion on the physiological absorption is strongly indicated.

According to the contact depletion theory of Jenny and Overstreet (9), plants might cease to accumulate ions at very low degrees of saturation and actually give off ions to the clay particles. This *critical degree of K saturation* was not reached in the present study, indicating that for the systems under consideration it must lie below 10 per cent potassium. Tiulin (11), who studied the availability of adsorbed phosphates, also has postulated a critical degree or zone of saturation. According to Tiulin, it is that degree of saturation below which the adsorbed ions remain unavailable to the plant. It should be pointed out, however, that on the basis of the soil solution theories, nutrients are available at all degrees of saturation, although, of course, to a lesser extent as *D* becomes smaller (fig. 1). The critical degree of saturation is most sharply defined by the contact exchange theory, according to which the roots accumulate elements above the critical degree of saturation and loose them below it. We believe that the critical degree of saturation is not a fixed property of the soil but depends on the type of plant and its physiological conditions.

From the viewpoint of agricultural practice, it is of interest to note that Ca is the least retarding cation in the process of liberation of potassium, a fact which again demonstrates the superiority of neutral, calcium-saturated soils. As a matter of fact, neutralizing an acid soil with Ca should render K more available, as indicated by a comparison of the K-H-curve and the K-Ca-curve. New light is shed on the problem of soil acidity. As soils gain hydrogen ions the remaining nutrient ions not only are reduced in numbers but become less exchangeable; in other words, less available for consumption by plants. Plant production suffers correspondingly. These relationships very likely play a more important part in the problem of soil acidity than the direct toxic effects of hydrogen ions in soils, for which no convincing direct physiological influence has as yet been demonstrated. It is probable that similar relationships exist in many alkali soils (Na-soils) in which Na ions constitute the bulk of the complementary cations. For equal applications of potassium fertilizer, crops should utilize a higher percentage from light-textured than from heavy-textured soils. The high exchange capacity of heavy soils brings about a low degree of saturation of potassium. The reverse is true for light

soils: the exchange capacity is low, and equal numbers of K ions make up a high percentage of the exchangeable ions. The practical consequences of these inverse relationships have been discussed in great detail by Vageler (14).

Although we have placed emphasis on the degree of saturation, we are, of course, fully aware of the importance of the magnitude of the absolute amount of exchangeable K in the soil for plant production. This is the value usually determined by extraction methods with the aid of neutral salts or dilute acids (e.g., quick tests). It appears in the equation as b_0 . Our studies demonstrate, however, that the physiological availability of the absolute K level depends on its degree of saturation and the nature of the complementary cations.

SUMMARY

A quantitative theory has been developed which relates base exchange to the degree of saturation. The exchangeability of adsorbed K decreases with decreasing degree of saturation. The nature of the complementary ions markedly affects these relationships.

The physiological availability of adsorbed potassium was investigated with the aid of excised barley roots. Corresponding studies were made with true solutions containing potassium ions. In this manner, it was possible to separate K intake into the colloid chemical exchange phase and the biological accumulation phase.

Lowering the degree of saturation of K resulted in a reduced intake of the element. In accordance with the exchange theory, the rate of decline was greatly affected by the nature of the complementary cation. Calcium was least effective; ammonium had the greatest influence; and hydrogen and sodium occupied intermediate positions.

Certain practical applications are discussed.

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THE EFFECT OF NATURAL GAS ON THE GROWTH OF MICRO-ORGANISMS AND THE ACCUMULATION OF NITROGEN AND ORGANIC MATTER IN THE SOIL

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When natural gas diffuses slowly into moist soil and the temperature is not extremely low, a white or light-colored residue soon appears on the surface of macroscopic openings occurring in the exposed area. During dry or cool weather, the color of this residue gradually changes to dark brown or black. This effect was observed by Schollenberger (5), who found, on examining a soil through which natural gas had escaped from a leak in a pipe line, that the soil exposed to the gas was dark brown and emitted an acrid odor similar to that of mud beneath stagnant water. A chemical analysis indicated that the affected soil was higher in replaceable ammonia and exchangeable manganese than was soil from an adjacent area which had not been exposed to the gas. A qualitative test of soil taken from the affected area and maintained for 6 weeks in a partially enclosed container at a favorable moisture content, indicated the presence of an abundance of nitrates. Wheat made a better growth in pots filled with soil which had been exposed to the gas than in pots containing normal soil.

Eight samples of natural gas from Oklahoma were analyzed by Burrell and Oberfell (2). Methane was the most abundant hydrocarbon present, ethane occurred in some samples, and small quantities of propane and butane were also present. No hydrogen, carbon monoxide, hydrocarbons of the olefin series, or hydrogen sulfide was found by quantitative tests. Tausz and Donath (6) have isolated soil organisms which oxidize paraffin hydrocarbons; consequently these microorganisms might be expected to develop in soils where natural gas was present in sufficient quantities to provide a source of energy and where other conditions were favorable for growth. Giglioli and Masoni (3) conducted experiments on the absorption of methane in the presence of oxygen by the methane bacteria of Kaserer and Söhngen. They found that these organisms were more numerous in the deeper parts of the soil and that the optimum temperature for growth was 30°C. They suggested that the absorption and partial transformation of methane into fixed organic material is constantly adding to the fertility of the soil.

Other investigators, according to McBeth and Scales (4), found that methane is produced directly or indirectly from the decomposition of manure and the fermentation of cellulose. In their investigations, methane was formed only

under anaerobic conditions and in highly nitrogenous media by cellulose-decomposing organisms. Methane was produced in the absence of nitrates by a methane bacillus. More recent studies have been made by Barker (1) and others on methane production and utilization by microorganisms.

EXPERIMENTAL

When natural gas escapes into a soil in sufficient quantities, grass, trees, or shrubs growing on that area are killed. In the fall of 1927, a gas line was laid at a depth of 20 inches in a park in Stillwater, Oklahoma, and a leak occurred as a result of an imperfect connection. Bermuda grass planted in the spring of 1928 failed to grow on an area about 2 feet in diameter above the leak in the pipe line. After the leak was repaired, the grass made a luxuriant growth on this area in 1929, and the grass was darker green than that on adjacent soil which had not been exposed to the natural gas. A second observation was made along the south side of a small wheat field in the southwest corner of the campus of the Oklahoma A. and M. College. A gas line was laid along the

TABLE 1

Effect of leaking natural gas on the nitrogen content of soil collected near the horticultural shed on the campus of the Oklahoma A. and M. College

SOIL NUMBER	DESCRIPTION	TOTAL NITROGEN
		<i>per cent</i>
1	Undisturbed soil at pipe level	.070
2	Surface soil 0"-8" deep	.115
3	Soil in ditch above gas leak	.121
4	Soil collected around pipe and exposed to gas	.142
5	Very dark soil near gas leak	.467

edge of this field in 1926, and gas escaped in numerous places around the couplings. The land was plowed about 4 years after the line was installed, and very dark masses of soil were observed where gas leaks had occurred. Wheat planted on the soil was killed, or growth was stunted in these areas. A sample of soil collected from one location where gas had escaped was analyzed for total nitrogen and was found to contain 0.22 per cent of this element as compared with 0.16 per cent in the soil which was not affected by the gas. Other soil samples collected in the vicinity of a gas leak near the horticultural shed on the campus of the Oklahoma A. and M. College were analyzed for total nitrogen. The results, shown in table 1, also indicate that the nitrogen content of soil is increased by exposure to small quantities of natural gas escaping from a pipe line.

In order to determine whether this accumulation of nitrogen might be due to ammonia occurring in the natural gas, duplicate analyses were made by measuring 105 cubic feet of gas with a standard gas meter and passing it

through a gas-absorption tower containing dilute sulfuric acid to absorb any ammonia which might be present. The ammonia was determined by distillation and absorption in standard acid and was rechecked in a second distillation with Nessler's reagent. Less than 0.01 p.p.m. of ammonia was present in the samples. Other analyses which have been made on natural gas do not indicate that ammonia is present; consequently, it is quite improbable that an increase in the nitrogen content of a soil could be due to the absorption of ammonia from the natural gas escaping slowly into it from a leaking pipe line.

When a close examination is made of soils exposed to small quantities of natural gas, colonies of microorganisms can be seen in various stages of development, depending upon temperature and moisture conditions. White masses of slime molds are usually abundant, and myxomycetes are frequently present. A sample of soil taken about 18 inches below the surface of an area near Stillwater, Oklahoma, where gas had slowly escaped from a pipe line for several years was examined by Elizabeth McCoy.¹ She found that *Clostridium butyricus* was abundant and that other species of *Clostridium* were also present. Since these organisms are capable of fixing atmospheric nitrogen, it is logical to expect that hydrocarbons in the natural gas would supply the necessary energy either directly or indirectly for the growth and development of these microorganisms, and as a result the nitrogen content of the soil would be increased. Another sample of "gassed" soil was sent to Frances E. Clark,² and the following report was obtained:

Several species of obligate anaerobes were found in dilutions up to one in ten thousand. *Clostridium sporogenes*, *Clostridium bifermentans*, and a round terminal-spored *Clostridium* were most readily recovered; the final identification of further species has been delayed by the presence of a large number of facultative anaerobes. Certain facultative species have been found in numbers of from 100,000 to 500,000 per gram. *Aerobacillus polymyxa* and *Aerobacillus macerans*, as well as *Bacillus brevis*, *Bacillus circulans*, and *Bacillus amylolyticus*, have been identified. The common aerobic *Bacilli* found predominantly in certain field soils recently studied were far from predominant in the soil submitted, for which the combined number of *Bacillus mycoides*, *Bacillus cereus*, and *Bacillus megatherium* was less than 100,000 per gram. Thus, although no control sample from adjacent normal soil was available for the spore-formers there appears to be a shift from the aerobic toward the facultatively anaerobic species.

After it appeared that nitrogen fixation was occurring in soils exposed to natural gas from leaking pipe lines, additional samples of soil were collected from several locations near Stillwater, Oklahoma, where gas had escaped or was escaping, and samples of normal soil taken from the same locality were analyzed for total nitrogen and organic matter. The results of these analyses are given in table 2.

In every soil which had been exposed to a slow infiltration of gas for a considerable length of time, the nitrogen content was increased. In some in-

¹ Department of bacteriology, University of Wisconsin.

² Division of Soil Microbiology, Bureau of Plant Industry, U. S. Department of Agriculture.

stances, the total nitrogen in very poor soils affected by gas was much higher than that occurring normally in some of the best soils in Oklahoma.

The average nitrogen and organic matter contents of the soils affected by gas were nearly three times as great as those of normal soils. The organic matter-nitrogen ratios of these soils were variable. The lowest ratio occurred in a "gassed" soil, and seven of the ten samples collected near gas leaks had lower ratios than the corresponding samples of soil not exposed to the natural gas. A narrow ratio would be expected from residues accumulating from micro-

TABLE 2

Effect of natural gas and growth of anaerobic organisms on the nitrogen and organic matter content of soils near Stillwater, Oklahoma

SOIL NUM- BER	LOCATION	TOTAL NITROGEN		ORGANIC MATTER		ORGANIC MATTER- NITROGEN RATIO	
		Normal soil	Gassed soil	Normal soil	Gassed soil	Normal soil	Gassed soil
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		
1	Oklahoma A. & M. College Campus South of Home Economics Building	.073	.195	2.18	4.95	29.9	25.4
2	Oklahoma A. & M. College Campus East of Horticultural Shed	.042	.085	0.77	1.44	18.3	16.9
3	Oklahoma A. & M. College Campus NW of Agri. Engineering Building	.042	.398	0.77	3.61	18.3	9.1
4	1 mi. N.; 1 mi. W. of Stillwater, Okla- homa	.164	.218	2.78	5.00	17.0	22.9
5	3½ mi. E.; 2 mi. S. of Stillwater, Okla- homa	.057	.270	1.21	3.04	21.2	11.3
6	4½ mi. E.; 2 mi. S. of Stillwater, Okla- homa	.061	.264	1.34	3.44	22.0	13.0
7	6½ mi. E.; 2 mi. S. of Stillwater, Okla- homa	.304	.425	3.24	11.65	10.7	27.4
8	7 mi. E.; 2 mi. S. of Stillwater, Okla- homa	.076	.284	0.88	2.99	11.6	10.5
9	8½ mi. E.; 2 mi. S. of Stillwater, Okla- homa	.115	.130	1.24	2.27	10.8	17.5
10	8½ mi. E.; 2½ mi. S. of Stillwater, Okla- homa	.042	.398	0.77	3.61	18.3	9.1
Average.....		.098	.267	1.52	4.20	17.8	16.3

organisms unless some free carbon might accumulate. The very narrow ratio of the unaffected soils needs further study to determine what factors may be responsible for this condition.

An experiment to determine the availability of the nitrogen accumulating in these "gassed" soils was conducted in the greenhouse. Soils collected near the gas leaks and similar soil which had not been affected by the escaping gas were placed in gallon cans, and oats were planted in them. The oat leaves were darker and more forage was produced by the plants in the "gassed"

soil as compared with plants in the normal soil. Data on yield were lost through failure of the thermostatic control on the drying oven.

Additional soil samples collected in or near Oklahoma City, Oklahoma, to obtain further information on the effects of escaping natural gas on the nitrogen and organic matter in soil were analyzed for these constituents. The results are given in table 3. The average nitrogen content of the soils exposed to natural gas was about two and one-half times as great as that of soil taken from an adjacent area which had not been affected, and the organic matter content of the "gassed" soils was nearly three times as high as that of the normal soils.

The organic matter-nitrogen ratios of these soils, like those of the Stillwater soils, were variable. No explanation can be given for the very high ratio in

TABLE 3

Organic matter and nitrogen content of soil samples collected from normal soil and from areas exposed to natural gas from leaking pipe lines in or near Oklahoma City, Oklahoma

SOIL NUM- BER	LOCATION	TOTAL NITROGEN		ORGANIC MATTER		ORGANIC MATTER- NITROGEN RATIO	
		Normal soil	Gassed soil	Normal soil	Gassed soil	Normal soil	Gassed soil
		per cent	per cent	per cent	per cent		
1	West Reno Street	.126	.297	2.75	10.60	21.8	35.7
2	20 ft. south of No. 1	.126	.291	2.75	10.40	21.8	35.7
3	SW $\frac{1}{4}$ Sec. 36, T 12 N, R 4 W	.102	.197	2.47	7.30	24.2	37.1
4	Portland Ave. and Frisco R. R.	.060	.357	1.95	7.96	32.5	22.3
5	Portland Ave. and 23th Street	.044	.129	1.60	4.60	36.4	35.7
6	Portland Ave. and 56th Street	.112	.258	2.67	8.25	23.8	32.0
7	Portland Ave. and 63rd Street	.028	.157	1.10	5.60	39.3	35.7
8	E $\frac{1}{2}$ Sec. 22 T 10 N, R 4 W	.073	.260	2.60	3.37	35.6	13.0
9	400 ft. south of No. 8	.151	.157	5.40	5.60	35.8	35.7
10	63rd St. and Santa Fe	.044	.134	1.40	4.80	31.8	35.8
11	1 mi. N. of Cushing, Oklahoma	.036	.092	1.24	4.71	34.4	51.2
12	1 mi. N. of Cushing, Oklahoma	.101	.106	2.75	3.70	27.2	34.9
Average.084	.203	2.39	6.41	30.4	33.7

some of the normal soils. One of the "gassed" soils had a low organic matter-nitrogen ratio, but the majority of the soils had very high ratios as compared with those of samples collected near Stillwater. Whether carbon has accumulated in these soils or whether organic compounds having a wide carbon-nitrogen ratio were produced by other microorganisms which were present was not ascertained in this study.

It is not improbable that nitrogen accumulation observed in many areas of idle land may be due to nitrogen fixation occurring as a result of the growth of microorganisms during periods when anaerobic soil conditions prevail. When natural gas was passed rapidly through soil placed in containers in the laboratory, moisture was removed and no apparent growth of microorganisms

occurred. In order to study the growth of microorganisms under controlled conditions, several samples of soil were treated with different fertilizers and placed in quart jars each containing a thin layer of white sand in the bottom. One liter of natural gas was passed into each jar every day through a glass tube which extended into the sand. After 5 weeks, the soils were examined, and slight development of microorganisms was observed. Further study is needed to determine the optimum environmental conditions for nitrogen fixation when natural gas passes slowly through soil.

SUMMARY

Observations of areas where natural gas was escaping from leaking pipe lines into the soil indicated that microorganisms were active when moisture and temperature were favorable for growth.

Dark-colored residues accumulate in soils exposed to natural gas and remain for several years after the gas leaks are repaired.

Analyses of soil samples for total nitrogen indicate that a marked increase of this element occurs in the affected areas. Species of *Clostridium*, which are capable of fixing nitrogen under anaerobic conditions, were present.

The organic matter-nitrogen ratio was not constant in samples collected from different areas. The exact cause of this condition was not determined.

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THE ADSORPTION OF PROTEINS BY MONTMORILLONITIC CLAYS¹

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Soil organic matter has several characteristics which suggest that it may be combined with the clay fraction of the soil. Its resistance to oxidation in clay soils, its immobility in clay soils, and the difficulties involved in separating the organic and inorganic soil colloids in the laboratory, are observations which indicate that a combination may exist between these two fractions. The investigations of Demolon and Barbier (1), Mattson (3), Meyers (4), and Giesecking (2) show that various organic substances have a tendency to react with clays. According to Demolon and Barbier, humic colloids are strongly adsorbed by clay when the hydrogen-ion concentration of the system is high. Mattson found the isoelectric point of proteins to be lowered by the addition of bentonite. He explained this change by suggesting that bentonite forms a nonionized compound with proteins. Meyers observed that organic colloids mixed with inorganic soil colloids showed a reduction in cation exchange capacity from the sum of the capacities of the two components. He also observed that the tendency of organic colloids to combine with the inorganic soil colloids was greater in acid suspensions. He suggested polar adsorption as the probable reaction involved. Giesecking found complex organic cations to be strongly adsorbed within the variable portion of the (001) spacings of montmorillonitic clay crystals. These complex cations replaced the hydrogen from electrodialed montmorillonite, resulting in larger (001) spacings.

The chemical properties of the base-exchange clays and soil organic matter are of a nature that should permit combinations to exist between these fractions. The tissues of animals and plants contain most of their nitrogen in a basic form, or a form that becomes basic upon hydrolysis. Organic matter derived from these sources will be capable, therefore, of reacting like basic compounds. This should make possible a combination between the basic or positive spots of the organic matter and the acidic or negative spots on the crystal lattice of the clay. In fact, individual particles of soil organic matter will have a great number of positive spots resulting from free amino groups. Likewise, individual clay crystals, having a cation-exchange capacity, will have

¹ Contribution from the division of soil physics, department of agronomy, University of Illinois, Urbana, Illinois. Published with the approval of the director of the experiment station.

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a great number of negative spots. If the two particles should orient themselves in such a manner that there was a mutual attraction between many of these spots, a stable combination would be obtained. In this way the clay crystal might be covered by a "network" of organic material.

In the present study, albumen-montmorillonite and gelatin-montmorillonite complexes were prepared. The reactions were followed by measuring the change in the (001) spacings of the montmorillonite by x-ray diffraction methods. Montmorillonite was selected for this study because this type of mineral is one of the components of many of the clays possessing a high cation-exchange capacity. Proteins were selected because they are one of the most common of the nitrogenous substances added to soils.

EXPERIMENTAL TECHNIC

The montmorillonite was obtained by taking a fraction of Wyoming bentonite containing those particles less than $0.5\ \mu$ in diameter. The water suspension of this fraction was raised to approximately pH 10 by adding sodium hydroxide. Water suspensions of albumen and of gelatin were made and adjusted to the same pH by the same method. The concentration of the suspensions was determined by drying known volumes in an oven at 105°C . The first step in the preparation of the protein-montmorillonite complexes was the thorough mixing of an alkaline protein suspension with an alkaline montmorillonite suspension. In alkaline suspension, both the montmorillonite and the protein are negatively charged, with the result that the two substances are not mutually attracted to any great extent. Under these conditions a homogeneous mixture is easily obtained. The final step in the preparation of the complex was the acidification of the mixed suspension. The montmorillonite remains negatively charged while the protein becomes positively charged when the pH of the suspension becomes lower than its isoelectric pH. Under these final conditions the protein and montmorillonite mutually attract each other and are completely flocculated. All of the suspensions were acidified gradually by adding dilute acetic acid. This was followed by adding concentrated acetic acid where low pH values were desired. The acidified suspensions were shaken in a mechanical shaker for 48 hours. The flocculated protein-montmorillonite complexes were then filtered, washed with water, and dried over anhydrous magnesium perchlorate.

Three series of protein-montmorillonite samples were prepared. In one series the amount of gelatin per gram of montmorillonite was varied. In this series, the final pH of the mixed suspensions was adjusted to 2.6. In a second series, the amount of albumen per gram of montmorillonite was varied, and the final pH of the suspension was adjusted to 2.6. In the third series, 1 gm. of gelatin was added to each gram of montmorillonite in the suspension. In this series, the final pH of the suspension was varied.

A powder x-ray diffraction pattern was made from each of the dried samples. The samples were exposed in a closed system over anhydrous magnesium

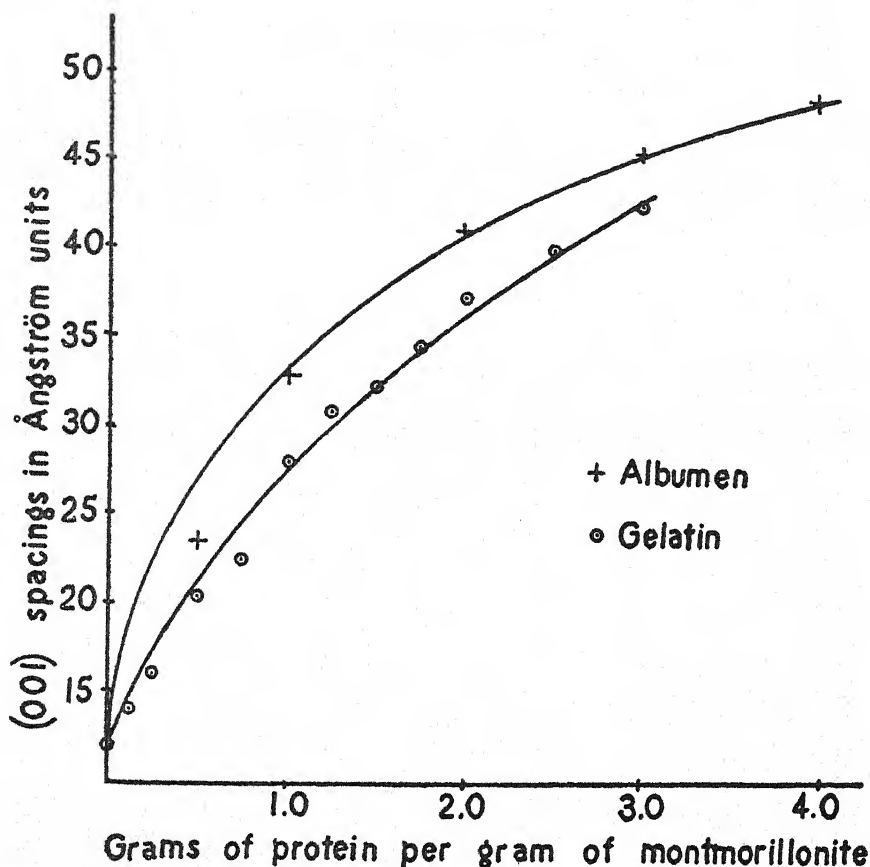


FIG. 1. EFFECT OF VARIOUS AMOUNTS OF ADSORBED PROTEINS ON THE (001) SPACINGS OF MONTMORILLONITE

TABLE 1

Effect of hydrogen-ion concentration on the adsorption of gelatin by montmorillonite

FINAL pH OF THE SUSPENSION DURING PREPARATION	(001) SPACINGS OF MONTMORILLONITE TREATED WITH GELATIN*
	Å.
7.0	23.0
5.5	25.7
4.0	27.0
2.7	26.9
1.0	26.9

* 1 gm. gelatin to 1 gm. montmorillonite.

perchlorate. $\text{FeK}\alpha$ radiation was used. The diffracted radiation was recorded on a flat film at a distance of 5 cm. from the sample.

EXPERIMENTAL RESULTS

The (001) spacings of montmorillonite samples treated with varying quantities of albumen and those of another series treated with gelatin are plotted in figure 1. X-ray diffraction patterns of the gelatin-montmorillonite series are reproduced in plate 1. The effect of the hydrogen-ion concentration on the adsorption of gelatin by montmorillonite is shown in table 1.

DISCUSSION OF RESULTS

The data presented in figure 1 and the x-ray diffraction diagrams in plate 1 show that the (001) spacings and the intensity of diffraction from the (001) planes of montmorillonite gradually increase upon the addition of increasing amounts of protein. This change in the (001) spacings and (001) planes shows that the large protein molecules are being adsorbed within the variable portion of the (001) spacing of the crystal lattice.

The results in table 1 show that the hydrogen-ion concentration of the suspensions during preparation is important in determining the degree of adsorption of proteins by montmorillonite. The adsorption is more nearly complete when the hydrogen-ion concentration is high. This indicates that the protein is being adsorbed as cations. The high hydrogen-ion concentration results in an increase in the degree of ionization of the amino or basic groups and at the same time represses the ionization of the acidic groups of the protein molecules. Under these conditions the amphoteric protein molecule tends to act as a cation, and the tendency to act as an anion is diminished.

In order to determine more of the nature of the adsorption of proteins by montmorillonite, the adsorption of gelatin treated with nitrous acid was compared to the adsorption of untreated gelatin. Nitrous acid destroys the free amino groups of proteins, thereby rendering them non-basic. In this experiment 1 gm. of gelatin was added to 1 gm. of montmorillonite in each case. The montmorillonite complex with untreated gelatin had a (001) spacing 8.0 Å. greater than the complex with the nitrous acid treated gelatin. The treated gelatin was still polar, and for this reason showed evidence of adsorption by the montmorillonite; but the untreated gelatin, which was capable of reacting as a cation, was more completely adsorbed.

SUMMARY

X-ray diffraction data obtained in this investigation show that albumen and gelatin are adsorbed within the characteristic expansible portion of the montmorillonite crystal lattice. These proteins are more completely adsorbed in suspensions with high hydrogen-ion concentrations than in suspensions with low hydrogen-ion concentrations. Untreated gelatin was more completely adsorbed than gelatin treated with nitrous acid to destroy its basic properties. These observations suggest that the adsorption of proteins as cations is partly responsible for their combinations with montmorillonite.

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PLATE 1

X-RAY DIFFRACTION DIAGRAMS OF SAMPLES OF MONTMORILLONITE TREATED WITH VARIOUS
AMOUNTS OF GELATIN IN SUSPENSIONS ADJUSTED TO pH 2.6

Ratio of gelatin to
montmorillonite

(001) spacings in
Ångström units

0.25 to 1.00

16.0

0.50 to 1.00

20.5

0.75 to 1.00

22.5

1.00 to 1.00

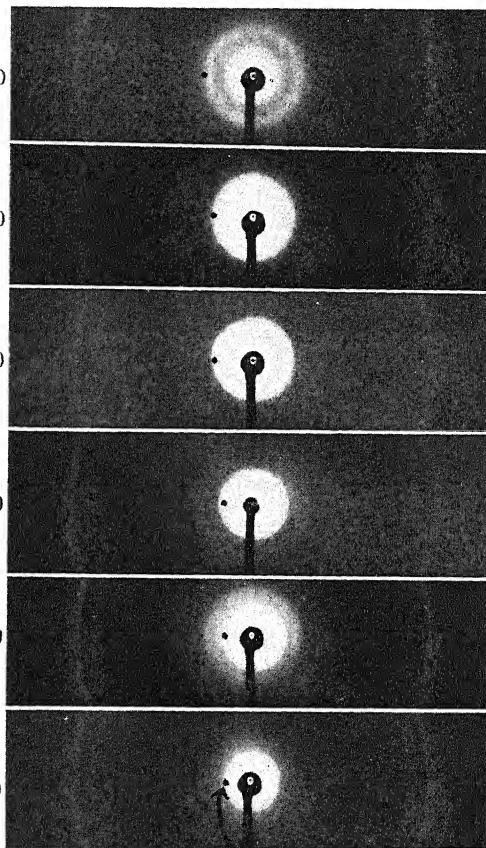
28.0

1.50 to 1.00

32.2

2.00 to 1.00

37.3



(001) diffraction line

DISPERSION OF LATERITIC SOILS AND THE EFFECT OF ORGANIC MATTER ON MECHANICAL ANALYSIS¹

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One of the important physical determinations made in connection with studies of soil erodibility is the mechanical analysis. In making mechanical analyses of lateritic soils some difficulties were experienced in obtaining complete dispersion, a fact which led to an investigation of the effectiveness of different dispersing agents. It was also observed that most of these soils contained very little organic matter; it was thought advisable, therefore, to test the effect of omitting the hydrogen peroxide pretreatment for removing organic matter in order that this time-consuming operation might be eliminated in routine work if it was found to be unnecessary.

DISPERSION OF SOILS

The dispersion of lateritic soils was studied after flocculation was encountered during mechanical analysis when sodium oxalate was used as the deflocculent. Alexander (1), noting that the clay fraction of lateritic soils dispersed with sodium oxalate frequently flocculated, suggested that in such cases sodium hydroxide be used in making mechanical analyses. He found no indication of flocculation in sodium hydroxide suspensions after these samples had been allowed to stand for 4 weeks. The results obtained in this laboratory also showed that sodium oxalate suspensions were very unstable. The principal disadvantage of using sodium hydroxide alone is the difficulty of making an accurate correction for the weight of dispersing agent present in the suspension. The value for the correction varies considerably from one determination to another, although the same concentration of sodium hydroxide is used.

Steele and Bradfield (7) dispersed soils with sodium oxalate alone and with sodium hydroxide alone after removing the bases by electrodialysis, and showed that the clay content was higher in the soils dispersed with sodium oxalate. Bouyoucos (2) dispersed soils with a combination of sodium oxalate and sodium hydroxide

Preliminary tests showed that satisfactory dispersion was obtained by using 5 ml. of 0.5 *N* $\text{Na}_2\text{C}_2\text{O}_4$ and 3 ml. of *N* NaOH per liter of suspension containing

¹ Contribution of the Soil Conservation Service in cooperation with the South Carolina Agricultural Experiment Station.

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10 gm. of soil (plate 1). This combination gave stable suspensions, and the variation of the correction for the weight of dispersing agent present in the suspension was very small. Blanks to determine the correction for the weight of dispersing agent always gave approximately the same values, which were relatively close to the theoretical values.

Table 1 shows the mechanical analyses of some lateritic soils dispersed with sodium oxalate alone and with the combination of sodium oxalate and sodium hydroxide. Comparisons of the clay contents obtained clearly show that flocculation occurred in several of the samples dispersed with sodium oxalate. The B horizons of most samples apparently flocculated more readily than the A horizons when sodium oxalate was used alone. The silt fractions show a marked decrease and the clay fractions a large increase when the flocculated

TABLE 1

Mechanical analyses of lateritic soils dispersed with sodium oxalate alone and with combined sodium oxalate and sodium hydroxide

SOIL TYPE	HORIZON	DISPERSED USING 10 ML. 0.5 N $\text{Na}_2\text{C}_2\text{O}_4$			DISPERSED USING 5 ML. 0.5 N $\text{Na}_2\text{C}_2\text{O}_4$ + 3 ML. N NaOH		
		Sand	Silt	Clay	Sand	Silt	Clay
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Cecil sandy clay loam.....	B	31.61	10.92	59.25	30.51	9.35	61.41
Cecil sandy clay loam.....	B	34.05	53.25	15.36*	33.73	11.76	56.02
Cecil sandy loam.....	B	32.79	15.26	44.25*	33.36	11.10	57.33
Cecil sandy clay loam.....	B	36.46	66.04	3.36*	33.51	12.09	55.52
Cecil sandy loam.....	B	25.30	12.10	64.72	24.83	10.86	65.41
Cecil sandy loam.....	A	76.63	13.39	10.64	75.84	11.44	12.21
Cecil sandy loam.....	A	88.67	8.02	6.41	85.49	8.41	6.81
Cecil sandy loam.....	B	47.96	10.32	43.71	47.40	9.32	44.58
Cecil sandy loam.....	B	40.26	13.65	48.17*	38.92	11.49	50.38

* Visible flocculation occurred during sedimentation in less than 8 hours.

samples were dispersed with the mixture of sodium oxalate and sodium hydroxide instead of the sodium oxalate alone.

Mechanical analyses have been made on about 200 samples of lateritic soils dispersed with the mixture of sodium oxalate and sodium hydroxide, and the results have been very satisfactory.

EFFECT OF ORGANIC MATTER

The necessity of eliminating the organic matter by pretreating the soil with hydrogen peroxide, as a preliminary step to mechanical analysis, was questionable. This pretreatment tends to make the procedure for mechanical analysis long and tedious. Hydrogen peroxide treatment and the number of washings necessary to free the soil of organic matter brought into solution by the peroxide limited the number of analyses to eight samples in duplicate a week. By

omitting the peroxide treatment and subsequent washings, the number of analyses which could be made during a week was more than trebled.

In making mechanical analyses of heavy alkaline soils, Joseph and Snow (4) omitted both the hydrochloric acid and the hydrogen peroxide pretreatments. They reported results on soils of high organic matter and high calcium carbonate content, and concluded that no soils encountered had required the removal of the organic matter.

Robinson (6) showed that in order to break down the mineral particles cemented together by the organic matter, it was necessary to pretreat soils to remove the organic matter. He found that in every case when the organic material was oxidized, the amount of clay and the degree of dispersion of the soils were increased.

The action of H_2O_2 on weathered mica was studied by Drosdoff and Miles (3). The result of the hydrogen peroxide treatment on weathered mica of the unhydrated type showed that the larger pieces were disintegrated, thereby increasing the amount of finer material and decreasing the coarser fractions. Mechanical analyses of soils high in mica content would probably be affected significantly.

Two methods of mechanical analysis of soils were adopted by the First International Soil Science Congress (8). One of these incorporated the hydrogen peroxide pretreatment to remove organic matter, and the other omitted it.

Data presented in table 2 show a comparison of results obtained when soils were pretreated with hydrogen peroxide and when the pretreatment was omitted. The pipette method was used in making the mechanical analysis, based on the procedure outlined by Olmstead, Alexander, and Middleton (5). The sand fraction was determined by difference when the method omitted the hydrogen peroxide pretreatment; and the sand fraction was weighed when the method included pretreatment.

All samples used were acid, having pH values between 4.65 and 6.63. The pH values were obtained by the glass electrode method. An attempt to correlate pH values with the quantity of dispersing agent required was not successful. Organic carbon was determined by dry combustion, and the percentage of carbon was multiplied by the factor 1.724 to obtain the values listed as percentage of organic matter. As the solution loss is not shown in table 2, a discrepancy may be noted when the percentages of sand, silt, and clay fractions for some samples treated with hydrogen peroxide are totaled. In some samples pretreated with H_2O_2 , however, it was noted that instead of a solution loss a slight gain in weight occurred. The sand fraction includes particles of 2.0 to 0.02 mm., the silt fraction 0.02 to 0.002 mm., and the clay fraction 0.002 mm. and smaller.

A comparison of the clay contents obtained by the two methods shows that they closely approach the same values. All values reported are averages of duplicates, which in no instance differed by more than 1 per cent. The mean difference between treatments shows that the values for the hydrogen peroxide

treated samples are slightly higher than the untreated samples, indicating that pretreatment with hydrogen peroxide does affect the amount of clay obtained.

TABLE 2

Comparison of mechanical analysis of lateritic soils with and without hydrogen peroxide pretreatment

SOIL TYPE	HORIZON	ORGANIC MATTER (C × 1.724)	SAND		SILT		CLAY	
			H ₂ O ₂ Treated	H ₂ O ₂ Omitted	H ₂ O ₂ Treated	H ₂ O ₂ Omitted	H ₂ O ₂ Treated	H ₂ O ₂ Omitted
			per cent	per cent	per cent	per cent	per cent	per cent
Cecil sandy loam.....	A	0.79	84.74	85.43	7.79	6.91	7.38	7.66
Cecil sandy loam.....	B	0.74	47.96	47.83	8.16	8.51	44.06	43.66
Cecil sandy clay loam.....	A	1.55	65.96	66.28	12.03	11.56	22.05	22.16
Cecil sandy clay loam.....	B	0.84	32.26	32.00	6.62	6.84	61.85	61.16
Cecil sandy clay loam.....	A	0.95	62.44	63.75	10.76	9.64	26.71	26.61
Cecil sandy clay loam.....	B	0.48	32.51	35.14	12.98	11.27	55.46	53.58
Cecil sandy loam.....	A	1.07	72.02	72.27	14.43	15.27	12.29	12.46
Cecil sandy loam.....	B	0.64	32.75	32.31	11.27	10.57	57.11	57.13
Cecil sandy loam.....	A ₁	0.57	89.61	90.38	5.99	6.09	3.87	3.53
Cecil sandy loam.....	A ₂	0.45	72.39	71.16	16.31	17.31	12.33	11.54
Cecil sandy loam.....	B	0.43	39.04	39.73	11.76	10.96	50.29	49.32
Cecil sandy clay loam.....	A	0.76	72.21	72.77	7.96	6.61	20.47	20.62
Cecil sandy clay loam.....	B	0.33	34.96	33.25	12.48	12.47	54.42	54.28
Cecil sandy loam.....	A	2.38	74.84	76.02	12.29	12.93	10.37	11.05
Cecil sandy loam.....	B	1.07	25.60	25.67	10.03	10.10	64.67	64.23
Cecil sandy loam.....	A	1.59	80.06	81.22	10.32	11.34	8.26	7.44
Cecil sandy loam.....	A	0.95	83.22	83.79	10.52	8.70	7.10	7.51
Cecil sandy loam.....	B	0.86	46.08	46.13	10.25	11.92	43.61	41.95
Cecil sandy loam.....	A	0.81	84.57	85.14	7.41	7.33	7.99	7.53
Cecil sandy loam.....	B	0.72	56.27	56.24	13.27	13.06	31.97	30.70
Susquehanna clay loam.....	A	2.62	53.51	55.52	12.38	10.27	36.50	34.21
Susquehanna clay loam.....	B	1.00	34.86	35.23	11.27	8.70	57.84	56.07
Greenville sandy loam.....	A	1.22	56.70	60.96	2.37	3.73	41.47	35.31
Greenville sandy loam.....	B	0.90	42.85	42.54	2.71	3.75	55.33	53.71
Orangeburg sandy loam.....	A	0.57	84.15	85.51	6.19	5.16	10.39	9.33
Orangeburg sandy loam.....	B	0.31	70.58	71.99	7.34	6.20	23.61	21.81
Ruston sandy loam.....	A	0.72	90.65	91.44	4.31	4.58	4.86	3.98
Ruston sandy loam.....	B	0.33	70.27	70.03	8.19	7.59	23.28	22.38
Iredell loam.....	A	1.52	63.70	65.83	19.82	19.21	16.38	14.96
Iredell loam.....	B	0.76	29.15	27.55	13.57	12.45	57.56	59.94
Davidson clay loam.....	A	1.98	53.96	57.05	15.88	15.45	29.44	27.49
Davidson clay loam.....	B	0.93	40.66	42.59	15.81	14.83	44.26	42.58
Mean difference between treatments.....				0.69		-0.35		-0.85
Standard error of mean differences.....				±0.23		±0.18		±0.24

There is apparently no definite relation between the organic matter content and the difference in clay values obtained by the two methods. The organic matter contents range from 0.33 to 2.62 per cent. Some samples with organic

matter above 1 per cent give, by both methods, results very close to the same values. Other samples which contain less organic matter show results more widely separated.

The mechanical analysis of most lateritic soils for practical purposes can probably be made by the method in which the hydrogen peroxide pretreatment is omitted, thereby saving much time. The thirty-two samples shown in table 2 were analyzed in less than a week when the pretreatment was omitted, whereas more than a month was required when they were pretreated with hydrogen peroxide. The omission of the hydrogen peroxide pretreatment is recommended for routine mechanical analyses on most lateritic soils.

SUMMARY

Flocculation occurred during mechanical analysis of some lateritic soils dispersed with sodium oxalate. The result was that the values obtained for the clay fractions were far too low. Stable suspensions were obtained by using a mixture of 5 ml. 0.5 N $Na_2C_2O_4$ and 3 ml. N $NaOH$.

The effect of organic matter on mechanical analysis was studied. Data presented on 32 samples of lateritic soils show that the clay contents are slightly higher when the organic matter is removed, the silt fractions are not significantly different, and the sand fractions of the samples untreated are higher. In view of the time and work saved and the small difference between the two methods, it is concluded that the hydrogen peroxide pretreatment may be omitted for routine analyses of lateritic soils.

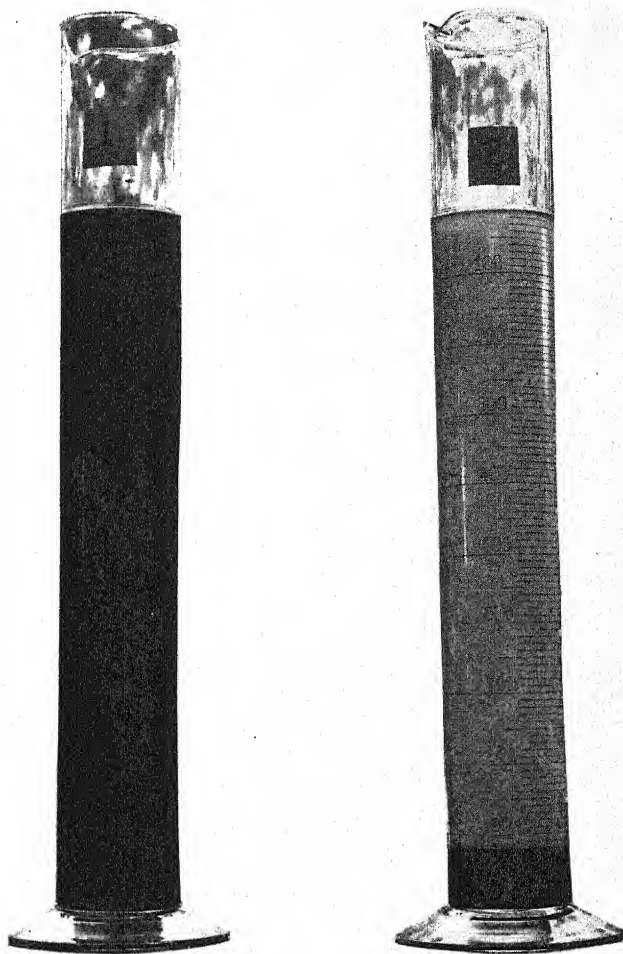
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PLATE 1

DISPERSION OF CECIL SANDY CLAY LOAM

The soil in cylinder 1 was dispersed with sodium oxalate plus sodium hydroxide; that in cylinder 2, with sodium oxalate only. Flocculation was visible in cylinder 2 after 1 hour of sedimentation. The photograph was made after 18 hours.



THE GENESIS OF DAVIDSON CLAY LOAM

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In our detailed investigations of the course of the changes between parent basic igneous rocks and their derived red earth soils, by means of silicate analysis and the application of dye tests [including our alizarin test (4)], representative samples of Davidson clay loam were examined along the lines of previous investigations into red earth formation in British Guiana (5) and Grenada (6). These samples, from a profile site in Chatham County, 50 miles west of Raleigh, North Carolina, are representative of (i) the parent rock at the 6-foot depth, (ii) its weathering crust, and (iii) the B horizon, or red earth, between the 20- and 24-inch depth, presumably derived from this weathered material.¹

DESCRIPTION OF THE SAMPLES

(i) The *parent rock* is a fine-grained dolerite (diabase) or basalt consisting of about equal parts of intercrystallized white basic feldspar, probably anorthite, and dark bluish green ferromagnesian minerals, probably mainly pyroxene. Magnetite and quartz are scarce or absent, but ilmenite is present in small amount. The pyroxene, in part, may be a titan-augite, because the total quantity of titania seems to be too great to be accounted for solely by ilmenite. The unaltered rock occurs as deep-seated boulders and comprises kernels of all sizes, resulting from "onion-weathering" of the parent lava. The outer parts of the boulders split readily into a series of concentric layers, more or less decomposed.

(ii) The *weathering crust* or outermost shell, 5 to 8 mm. thick, is a coherent, structureless, brittle, lemon-yellow, sandy material, which easily crumbles. It merges imperceptibly with the red earth in which the decomposing boulders are embedded.

(iii) The *red earth*, comprising the *B horizon*, is described in the Soil Survey Bulletin for Chatham County (7) as a "dark red or maroon, heavy, stiff but brittle, smooth clay," which "breaks into large angular pieces which readily break into small angular particles."

Davidson clay loam was selected in 1930 by Middleton (9) for full laboratory

¹ The writers wish to thank J. F. Lutz, associate professor of soils, North Carolina State College of Agriculture, Raleigh, N. C., for procuring material of the Davidson profile and for furnishing notes describing some of its features.

study as an example of a nonerosive soil. He describes the A horizon as reddish brown clay loam, 0 to 9 inches; the B₁ horizon, 9 to 36 inches, deep red, heavy brittle clay, breaking into large lumps that crumble into smaller angular and subangular fragments; the B₂ horizon, 36 to 60 inches, paler red, friable clay, overlying the C horizon, which consists of ocher-yellow, black, and reddish brown decomposition products of the parent rock. The laboratory data published by Middleton include complete physical and chemical analyses of material from the different horizons, as well as their colloidal components. Data appertaining to the chemical composition of the Davidson profile were also published by Anderson and Byers in 1931 (1) and discussed by them later in relation to soil classification (3). Colloidal fractions, four in number, were separated from the B₁ horizon material and chemically analyzed by Brown and Byers of the U. S. Bureau of Soils, who published their results in 1932, together with data for the fine and coarse silt fractions (2). The analytical results obtained by the Bureau of Soils investigators have been brought together and discussed by Marbut (8, p. 61, 62).

The climatic conditions now existing in the Southeastern States where Davidson clay loam has developed are subtropical, and the original vegetation was deciduous forest. The mean annual temperature is 60°F., the mean summer temperature 77°F., and the mean winter temperature 42°F.; the average annual rainfall is 44 inches, and the rain is fairly uniformly distributed throughout the year, though slightly greater in amount during the summer months.

DISCUSSION OF EXPERIMENTAL RESULTS

The same methods of examination were employed as those described fully in an article (6) on the red earth of Grenada, British West Indies. The results of chemical analysis are presented in table 1. The contents of quartz (determined by a tri-acid digestion method) are given separately from those of combined silica, and of free (gibbsitic) alumina (determined by the improved alizarin method) separately from those of combined alumina; similarly for the water of constitution of gibbsite as distinct from that of other hydrous minerals. This modification of the conventional method of presentation, by eliminating *free* oxide components, imparts much greater meaning to silica-alumina (and other) molecular ratios. Both the whole material and the colloidal clay fraction (2 μ downward) were chemically analyzed. Comparable data obtained by the Bureau of Soils investigators are also presented in table 1.

The losses and gains of each oxide component are shown in table 2, *total alumina being assumed to remain constant* throughout the transformations between rock and red earth. Computations from the data of the Bureau of Soils investigators are also given for comparison, but the composition of the weathering crust is not included in these data, since this material was not analyzed by those investigators; instead, the results of our analysis of the crust are employed for evaluating the changes between the crust and the C horizon of the soil.

TABLE 1
Bulk chemical composition of the Davidson red earth profile samples

Bulk chemical composition of the Dawson red earth profile samples

SAMPLE	PERCENTAGE COMPOSITION										MOLECULAR RATIOS*			
	SiO ₂		Al ₂ O ₃		Fe ₂ O ₃	TiO ₂	CaO	MgO	H ₂ O		SiO ₂ Al ₂ O ₃	Fe ₂ O ₃ Al ₂ O ₃	SiO ₂ H ₂ O	Al ₂ O ₃ H ₂ O
	Quartz	Combined	Gibbsitic	Com- bined					Gibbsitic	Other				
<i>Whole material†</i>														
(i) Rock.....	52.0	...	15.9	14.5	1.9	7.1	4.2	...	2.1	5.55	0.58	7.41	1.33
(ii) Crust.....	(15.0)	(26.7)	7.3	8.8	25.9	3.0	0.6	3.2	3.9	3.8	(5.15)	1.87	(2.11)	0.41
(iii) B Horizon.....	5.8	34.0	3.1	24.1	19.5	1.8	0.2	0.4	1.6	10.2	2.40	0.52	1.00	0.42
<i>Colloidal clay (2 μ downward)</i>														
(ii) Crust.....	1.1	23.1	10.7	14.4	32.2	1.4	tr.	0.8	5.7	8.7	2.73	0.70	1.26	0.29
(iii) B Horizon.....	0.4	33.0	7.0	22.8	21.6	1.4	tr.	0.5	3.7	8.9	2.47	0.60	1.11	0.45
<i>Analysis by U. S. D. A., Bureau of Soils</i>														
<i>Whole material</i>														
C Horizon.....	52.6	21.0	13.4	13.4	1.2	0.3	1.0	9.2	4.26	0.41	1.89	0.44
B ₂ Horizon.....	50.5	23.1	14.9	14.9	1.5	0.3	0.6	9.4	3.73	0.41	1.78	0.48
B ₁ Horizon.....	52.7	22.9	10.6	10.6	1.4	0.5	0.4	10.6	3.92	0.30	1.67	0.42
A Horizon.....	70.5	12.5	6.1	6.1	1.8	0.8	0.5	7.7	9.28	0.31	2.86	0.31
<i>Colloidal clay (1 μ downward)</i>														
C Horizon.....	35.2	29.7	20.1	20.1	0.9	0.5	0.1	12.5	2.02	0.43	0.96	0.48
B ₂ Horizon.....	35.4	29.4	20.6	20.6	1.0	0.4	0.4	12.3	2.04	0.45	0.98	0.48
B ₁ Horizon.....	36.9	31.7	16.0	16.0	0.9	0.6	0.4	13.1	1.98	0.32	0.97	0.49
A Horizon.....	34.4	32.1	12.4	12.4	2.0	0.6	0.9	17.1	1.82	0.25	0.73	0.40
Kaolinite.....	2.00	1.00	0.50

* Combined components (analysis by authors) and total components (analysis by U. S. D. A. Bureau of Soils).

† Sample (i), (ii), and (iii) were found to contain 0.024, 0.17, and 0.14 per cent MnO₂ respectively.

TABLE 2
Transformations between parent rock and weathering products of the Davidson profile
 Compositions recalculated to constant total alumina

ANALYSIS BY U. S. D. A., BUREAU OF SOILS INVESTIGATORS									
ANALYSIS BY AUTHORS					Percentage Composition				
Percentage Composition					Losses or Gains				
(i) Rock	(ii) Crust	(iii) B Horizon			(ii) Crust	(iii) B Horizon			
Percentage Composition					Losses or Gains				
(i) Rock	(ii) Crust	(iii) B Horizon	C Hori- zon	B ₁ Hori- zon	B ₂ Hori- zon	A Hori- zon	C Hori- zon*	B ₂ Hori- zon	A Hori- zon
Whole material									
Quartz.....	(15.0)	3.4	39.8	34.7	36.6	89.6	-1.4	-5.1	+1.9
Combined SiO ₂	(26.2)	19.9	15.9	15.9	15.9	15.9
Gibbsite.....	7.2	1.8	15.9	15.9	15.9	15.9
Combined Al ₂ O ₃	8.7	14.1	10.1	10.3	7.4	7.8	-15.5	+0.2	-2.9
Fe ₂ O ₃	25.6	11.4	10.1	10.3	7.4	7.8	-2.1	+0.1	0.0
TiO ₂	1.9	3.0	0.9	1.0	1.0	2.3	-0.4	0.0	+0.1
CaO.....	7.1	0.6	0.2	0.2	0.3	1.0	-0.4	0.0	+0.1
MgO.....	4.2	3.2	0.8	0.4	0.3	0.6	-2.4	-0.4	-0.1
H ₂ O.....
Gibbsitic.....	3.8	0.9	7.0	6.5	7.4	9.8	-0.6	-0.5	+0.9
Other.....	3.8	6.0
Totals.....	97.1	58.9	74.7	69.0	68.9	127.0	-22.4	-5.7	-0.1
.....	97.7	+58.1
Colloidal clay									
Quartz.....	0.7	0.2	18.9	19.1	18.5	17.0	+3.6	+0.2	-0.6
Combined SiO ₂	14.6	17.6	15.9	15.9	15.9	15.9
Gibbsite.....	6.8	3.7	15.9	15.9	15.9	15.9
Combined Al ₂ O ₃	9.1	12.2	10.8	11.1	8.0	6.1	-9.6	+0.3	-3.1
Fe ₂ O ₃	20.4	11.5	10.8	11.1	8.0	6.1	-0.4	0.0	0.0
TiO ₂	1.9	0.8	0.5	0.5	0.5	1.0	+0.3	-0.1	+0.1
CaO.....	7.1	tr.	0.3	0.2	0.3	0.3	-0.5	+0.2	0.0
MgO.....	4.2	0.5	0.0	0.2	0.2	0.5	-2.4	0.0	-0.1
H ₂ O.....
Gibbsitic.....	3.6	2.0	6.7	6.7	6.6	8.5	-2.4	0.0	-0.1
Other.....	5.5	4.8
Totals.....	62.1	53.0	53.1	53.7	50.0	49.3	-9.0	+0.6	-3.7
.....	97.7	-0.8

* From weathering crust.

By analogy with the British Guiana and the Grenada material, the weathering crust of the Davidson profile should be primary laterite. Insofar as this material contains free alumina (over 7 per cent) and a large amount of water of hydration (8 per cent) and is deficient in bases, it may tentatively be so regarded. The data in tables 1 and 2 reveal the changes that accompany the formation of (a) the weathering crust from diabase and (b) red earth from the crust, under the climatic conditions that have obtained in North Carolina.

Primary laterite formation

The development of the weathering crust from the parent rock evidently has been accompanied by a *loss of bases* and of *total silica*. The feldspar of the rock has apparently suffered complete decomposition, and part of its alumina has separated as crystalline *gibbsite* ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). Consequently, a fixation of water of hydration has occurred. There has been an apparent gain in total iron oxide and titania, doubtless accounted for by losses of other components.

For the purpose of determining the mineralogical composition of the weathering crust, a sample was fractionated into the usual texture grades, and each sand fraction "cleaned" by the Truog sulfide-oxalate method (10). The component mineral grains after separation into "heavy" and "light" by sedimentation in bromoform were then identified under the microscope. The main results are given in table 3.

Nearly 86 per cent of the crust is comprised of sand particles over 10μ in diameter. A considerable part of these consists of quartz, but the exact amount could not be determined because tri-acid digestion failed to break up completely the component silicate minerals; the treatment left a 27.1 per cent residue, of which 20.3 was removed by volatilization with hydrofluoric acid, though only about 15 per cent of this silica could be claimed as consisting of quartz.

The state of occurrence of iron oxide in the weathering crust was investigated by dye tests (6). The results are given in table 4.

From the results of the dye tests, the weathering crust evidently does not contain much free iron oxide, although it contains an appreciable quantity of active siliceous clay minerals.² Microscopical examination revealed the occurrence of large amounts (at least 50 per cent) of a *chloritic* mineral in the coarse and medium sand fractions of the weathering crust. This chlorite settled but slowly in bromoform, and sharp separation was not obtained; its specific gravity thus ranged between 2.8 and 2.9. Chemical analysis of a

² *Diamine sky blue* is strongly adsorbed by free hydrous iron oxides from its solution in alcohol containing boric acid, but not from its solution in alcohol containing phosphate, because the phosphate is preferentially adsorbed and "blocks" the uptake of the dye. Under similar circumstances, halloysite strongly adsorbs diamine sky blue, but the presence of phosphate does not diminish its uptake. On the other hand, *janus red* is not appreciably adsorbed by hydrous iron oxides but is adsorbed markedly by the clay minerals. Hence it is possible, by these two dye tests, to differentiate between different clay minerals, in particular, between hydrous iron oxides and iron-bearing clay minerals or aluminosiliceous clay minerals.

sample of the portion that settled from the coarse sand fraction gave SiO_2 , 25.9, Al_2O_3 , 15.4, FeO , 16.4, Fe_2O_3 , 11.4, TiO_2 , 13.4, CaO , 0.9, MgO , 6.7, H_2O , 10.0—total 100.1 per cent. Expressed in molecular proportions, these

TABLE 3
Mineralogical composition of Davidson profile
Materials treated with H_2S and acid oxalate before examination*

	(i) PARENT ROCK	(ii) WEATHERING CRUST (LATERITE)	(iii) B HORIZON (RED EARTH)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
<i>Texture analysis</i>			
Coarse sand.....($> 200 \mu$)	48.8	45.4	3.3
Medium sand.....($200-50 \mu$)	27.6	14.6	7.3
Fine sand.....($50-10 \mu$)	19.6	25.7	25.4
Coarse silt.....($10-5 \mu$)	0.6	0.6	3.8
Fine silt + clay.....($< 5 \mu$)	3.4	13.7	60.2
<i>Mineral separation</i> (Bromoform: sp. gr. 2.85)			
Coarse sand: Heavy residue.....	(46.0)	41.8	5.3
Light fraction.....	(54.0)	58.2	94.7
Medium sand: Heavy residue.....	6.9	4.3
Light fraction.....	93.1	95.7
Fine sand: Heavy residue.....	0.1	0
Light fraction.....	99.9	100.0
<i>Characteristic minerals</i>			
Coarse sand: Heavy residue.....	Augite, ilmenite	Chlorite	Leucoxene, iron oxide concretions
Light fraction.....	Felspar and glass	Chlorite, quartz	Quartz
Medium sand: Heavy residue.....	Augite, ilmenite	Chlorite	Leucoxene, iron oxide concretions
Light fraction.....	Felspar and glass	Chlorite, quartz	Kaolinitic mineral chiefly Some quartz
Fine sand: Heavy residue.....	(Nil)	(Nil)
Light fraction.....	Quartz	Kaolinitic mineral

* Parent rock ground.

figures indicate a ferromagnesian mineral of formula $4(\text{Mg} \cdot \text{FeO}) \cdot 2\text{Al}_2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 5\text{H}_2\text{O}$, which is similar to that of the leptochlorite, delessite. The mineral occurs in the crust mainly as bright grass-green, clear, irregular grains.

Many of the grains contain abundant rusty decomposition products, and their surfaces are deeply etched. It has doubtless been formed by the decomposition of the augite component of the basic igneous rock.

The *colloidal clay* fraction ($<2 \mu$) of the weathering crust is small in amount (less than 10 per cent), but its composition clearly indicates the nature of the further breakdown products, presumably derived in part from chlorite. It contains nearly 11 per cent of free (gibbsitic) alumina (16.4 per cent of gibbsite), but only 1 per cent of quartz (table 1). Its total iron oxide content is high (32.2 per cent), though only a relatively small amount of iron oxide appears to occur in the free state (diamine sky blue test, table 4). The clay stains heavily with janus red, indicating the presence of some active hydrous

TABLE 4
Results of dye tests on Davidson profile samples
Values in dye units absorbed per gram air-dry material

SAMPLE*	ALIZARIN UPTAKE†	DIAMINE SKY BLUE UPTAKE‡			JANUS RED UPTAKE
		Boric	Phosphatic	Difference§	
		Whole material			
(i) Rock.....	50
(ii) Weathering crust.....	72	106	42	50	199
(iii) B Horizon.....	30	528	202	265	988
		Colloidal clay			
(ii) Weathering crust.....	104	78	9	66	...
(iii) B Horizon.....	68	340	52	272	...

* All materials ground to pass a 100-mesh sieve.

† 1 gm. air-dry material ignited before dye test.

‡ By air-dry material.

§ Difference values corrected for dye uptake by phosphated halloysite.

clay mineral. In table 5 the mineralogical composition of the colloidal clay of the crust is computed in terms of secondary minerals.

Assuming all the combined alumina to occur as *kaolinite* ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), derived by the decomposition of the feldspar of the rock and amounting to 36.4 per cent of the weight of the colloidal clay, there still remains a residue (42.0 per cent) which presumably contains virtually all the iron oxide and the rest of the combined silica and water. Expressed in molecular proportions, the quantities of these constituents are as follows: Fe_2O_3 , 0.201; SiO_2 , 0.103; H_2O , 0.201; indicating an iron-bearing clay mineral of formula $2\text{Fe}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$. This formula is not coincident with that generally accepted for *hoeferite* ($\text{Fe}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) nor with that for *nontronite* ($\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$), but the fact that the ratios of $\text{Fe}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$ are those of the simple whole numbers 2:1:2, suggests that the substance is a definite mineral, the identity

and specific properties of which need to be established by further study. It may have been produced either by the decomposition of chlorite or directly from augite.

Red earth formation

The formation of the red earth comprising the B horizon of the Davidson profile, assuming no loss of total alumina (table 2), has involved the removal of large amounts of silica, both free as quartz, and combined in siliceous min-

TABLE 5
Transformations between parent rock and colloidal clay products of the Davidson profile
Compositions recalculated to kaolinite

	PERCENTAGE COMPOSITION			LOSSES OR GAINS	
	Kaolinite (ideal formula)	Weathering crust	B horizon	Weathering crust	B horizon
Nonquartz SiO ₂	46.6	63.9	57.0	+17.3	+10.4
Combined Al ₂ O ₃	39.4	39.4	39.4
H ₂ O.....	14.0	23.8	15.4	+9.8	+1.4
<i>Computation as minerals (assuming kaolinite formation)</i>					
<i>Crystalline components</i>					
Gibbsite (Al ₂ O ₃ ·3H ₂ O).....		16.4	10.7		
Kaolinite (Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O).....		36.4	57.6		
Quartz (SiO ₂).....		1.1	0.4		
Iron mineral (2Fe ₂ O ₃ ·SiO ₂ ·2H ₂ O).....		42.0	0	{ Fe ₂ O ₃ , 32.2 SiO ₂ , 6.2 H ₂ O, 3.6	
<i>Amorphous components</i>					
Free iron oxides (Fe ₂ O ₃).....		0	21.6	Loss,	10.6
Free silica (SiO ₂).....		0	6.2	From iron mineral	
Titania (TiO ₂).....		1.4	1.4	
Bases (K ₂ O, Na ₂ O, CaO, MgO).....		0.8	0.5	
Water, excess (H ₂ O).....		0	0.9	
Total.....		98.1	99.3		

erals. Much of the gibbsite (nearly 60 per cent) has disappeared, presumably through its *resilication into a secondary kaolinitic mineral* (probably halloysite), by analogy with the transformations of primary laterite to kaolinitic red earth in British Guiana and Grenada (5, 6). A further loss of bases, especially magnesia, and a considerable loss of total iron oxide and titania (16 per cent), have also occurred.

The red earth contains only 36 per cent by weight of sand ($>10 \mu$). More than 11 per cent of this sand is quartz, insoluble in tri-acid mixture. A large proportion (nearly 70 per cent) is crystalline halloysite or kaolinite, which is

deeply stained by janus red. Nearly 3 per cent of the particles rapidly settle in bromoform and consist mainly of black ilmenite, much altered into pale yellow, waxy *leucoxene*, giving a spotty appearance to the grains. Chemical analysis of a sample of heavy residue from the coarse sand fraction gave SiO_2 , 13.9, FeO , 22.2, TiO_2 , 63.1, CaO , 1.1—total 100.3 per cent. The rest of the heavy residue consists of tiny shotlike red concretions, probably hematite.

The state of occurrence of iron oxide in the red earth is entirely different from that in the weathering crust, as is clearly indicated by dye tests (table 4). Apparently nearly all of the oxide occurs as free red hydrous iron oxide, possibly mainly goethite.

The *colloidal clay* fraction ($<2 \mu$) of the red earth comprises a large part of the whole material, probably over 50 per cent (1). It consists chiefly of halloysite or kaolinite (58 per cent), together with hydrous iron oxide (22 per cent), which imparts a bright red color to the material (table 5). It also contains about 10 per cent of gibbsite, or virtually all the free alumina of the whole material, in addition to nearly 7 per cent of free silica, of which only 0.4 per cent is quartz, the rest presumably being hydrous silica, and $1\frac{1}{2}$ per cent of free titania.

A sample of the colloidal clay fraction of the red earth was subjected to the Truog sulfide-oxalate treatment (10), and the resulting clay, which was nearly white, was chemically analyzed. It gave SiO_2 , 36.8, Al_2O_3 (gibbsitic), 1.0, Al_2O_3 (combined), 30.3, Fe_2O_3 , 9.5 per cent, having a silica-alumina molecular ratio of exactly 2.00, which is that of halloysite. The loss of iron oxide caused by the treatment was 68 per cent, and the loss of silica, 27 per cent. Most of the free alumina (gibbsitic) was removed by the treatment.

The Davidson red earth is very similar in composition to the Demerara and Grenada red earths, in that it consists essentially of secondary kaolinitic material (65 to 75 per cent), stained red with hydrous iron oxides (10 to 20 per cent), and containing secondary quartz (3 to 6 per cent), with some residual gibbsite (5 per cent). For purposes of comparison between the Grenada and the Davidson profiles, the mineralogical composition of the weathering crusts and that of the red earths have been computed and brought together in table 6.

Comparison with Bureau of Soils results

The clay mineral forming the main component of Davidson clay loam is believed by Brown and Byers (2) to be kaolinitic, solely on the grounds that the silica-alumina ratio of the colloidal fraction is very nearly 2.0 (see table 1). Their data do not show, however, a partition of total alumina into free and combined alumina, which the writers' analyses have proved to be feasible. Allowing for free (gibbsitic) alumina, the silica-alumina ratios are seen from our analyses actually to be *greater than* 2.0 (nearer 2.5 for the B horizon and 2.7 for the weathering crust), which suggests that the aluminosiliceous component is *anauxite* or some other silica-rich mineral of the kaolin group, unless it be granted that the surplus silica is present as free hydrous silica.

Anderson and Byers (1) describe the Davidson soil as "lateritic" on account of the low silica-*sesquioxide* ratios. The writers have elsewhere (6) discussed the nomenclature of rock-weathering products, and in accordance with our findings, we would use this term only for describing materials in which the presence of notable amounts of gibbsite (or other form of free alumina) had definitely been proved and not merely inferred. The alizarin test has directly demonstrated the presence of this essential component, both in the weathering

TABLE 6

Comparison of mineralogical composition of weathering crusts and red earths of the Grenada and Davidson profiles

Approximate percentage composition, estimated from the laboratory data

COMPONENT MINERALS	GRENADA PROFILE	DAVIDSON PROFILE
<i>Weathering crust</i>		
Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$).....	39.1	11.2
Halloysite or kaolinite.....	29.3	10.0
Hydrous iron oxides.....	10.9	2.5
Secondary quartz.....	2.9	(15.0)
Hydrous silica.....	2.3	0.8
Titania (free).....	2.6	0.5
Other minerals.....	12.9 (magnetite)	(53.0) (Chlorite) (1.8)? (Leucoxene) 5.2 (Iron-silicate clay mineral)
Total.....	100.0	100.0
<i>Red earth</i>		
Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$).....	5.1	5.0
Halloysite or kaolinite.....	70.9	67.4
Hydrous iron oxides.....	11.2	15.8
Secondary quartz.....	2.9	6.2
Hydrous silica.....	0.0	3.3
Titania (free).....	1.3	0.8
Other minerals.....	8.6 (magnetite)	1.5 (leucoxene)
Total.....	100.0	100.0

crust and in the red earth of the Davidson profile, the approximate contents being 11 and 5 per cent respectively, in contrast to 39 and 5 per cent for the Grenada profile (table 6). The weathering crust, although lateritic in nature, should not unqualifiedly be called "laterite," because its content of free alumina is slightly less than 13 per cent, and its silica-alumina ratio is greater than 1.33 (6). The occurrence in it of a preponderant amount of chlorite, the paucity of free iron oxide, and the presence of a considerable amount of quartz, may

perhaps justify the name "chloritic quartzose laterite." Judged by chemical composition (tables 1 and 2), the material is evidently not identical with the C horizon sample analyzed by the Bureau of Soils investigators, which closely resembles the red earth. Its formation from the parent rock has not been accompanied by appreciable losses of main constituents except bases, a fact which contrasts it markedly with the true laterite crust derived from basic igneous rocks in the humid tropics (0.6 per cent loss between rock and crust in the Davidson profile as against 38.2 per cent loss of total constituents in the Grenada profile). Its development has mainly involved an internal rearrangement of constituent oxides, with the formation of characteristic new iron-bearing minerals, of which one (chlorite) is a well-known secondary product and the other is an unidentified siliceous clay mineral.

The B horizon material of the Davidson profile, being almost identical with that of the Grenada profile, would briefly be called "red earth" (6). Because it contains gibbsite as well as abundant free hydrous iron oxide, it might alternatively be designated "lateritic ferruginous clay."

The Bureau of Soils analyses indicate that Davidson clay loam has begun to show profile differentiation. The very high silica-alumina ratio, 9.3, for the A horizon of the whole soil may be accounted for on the assumption that silica has accumulated in the surface soil, presumably as quartz. The colloidal clay fraction of the A horizon exhibits a low ratio, 1.8, and a normal content of silica. As quartz was not determined separately, this assumption is merely conjectural. Its acceptance would lead to the conclusion that the Davidson soil is *podzolized*. The ratios involving iron oxide also furnish evidence of surface leaching and demonstrate the removal of iron compounds from the A horizon and their accumulation in the B₂ horizon, though not in the B₁ horizon. Though the formation of the parent material of the Davidson soil has evidently taken place from below, upward (parent rock, weathering crust, C horizon clay), the development of the profile has proceeded by downward leaching under acidic humic conditions; it thus may be regarded as a tropical podzolic process. In the British Guiana red earth, (5) profile differentiation has proceeded to a very much greater extent, the A horizon consisting of a thick layer of highly quartzose residual sand, and the profile closely resembling that of a true podzol.

SUMMARY AND CONCLUSIONS

This investigation is an attempt to trace the mineralogical and chemical transformations that proceed during the development of Davidson red clay loam from basic igneous rock occurring in North Carolina lying within the Piedmont Region.

The quantitative methods employed were chemical analysis of whole materials and clay fractions both after fusion and after tri-acid digestion (for quartz), and alizarin adsorption after ignition (for free alumina). The qualitative methods were adsorption of other dyes for identifying free hydrous iron

oxides and siliceous clay minerals, and simple mineralogical examination of texture fractions.

Samples of (i) parent basic igneous rock, (ii) yellow weathering crust, and (iii) B horizon red earth subsoil were examined, and the results were compared with less complete data obtained by Bureau of Soils investigators.

The formation of the weathering crust from the rock, and of the red earth from the crust as deduced from the laboratory results, is fully described and discussed.

The *crust* is a sandy material consisting essentially of chlorite, secondary quartz, and halloysite, together with gibbsite, which indicates its lateritic nature. Its colloidal fraction (less than 10 per cent of the whole) contains an unidentified iron-bearing clay mineral of probable formula, $2\text{Fe}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Its composition is contrasted with that of the laterite crust of decomposing basic igneous rocks occurring in British Guiana and Grenada which contains three times as much gibbsite and halloysite but no chlorite and much less quartz.

The *B horizon red earth* of the Davidson profile and of the British Guiana and Grenada profiles contains more than half its weight of colloidal matter and consists essentially of halloysite, stained red with free hydrous iron oxides, probably mainly goethite, together with some anhydrous hematite. It contains an appreciable amount of gibbsite and a little secondary quartz; the Davidson red earth also contains free hydrous silica.

The genesis of the halloysitic component of red earths is believed to be the resilication of gibbsite occurring in the weathering crusts, and chiefly derived from basic (lime-soda) feldspars occurring in the parent igneous rock.

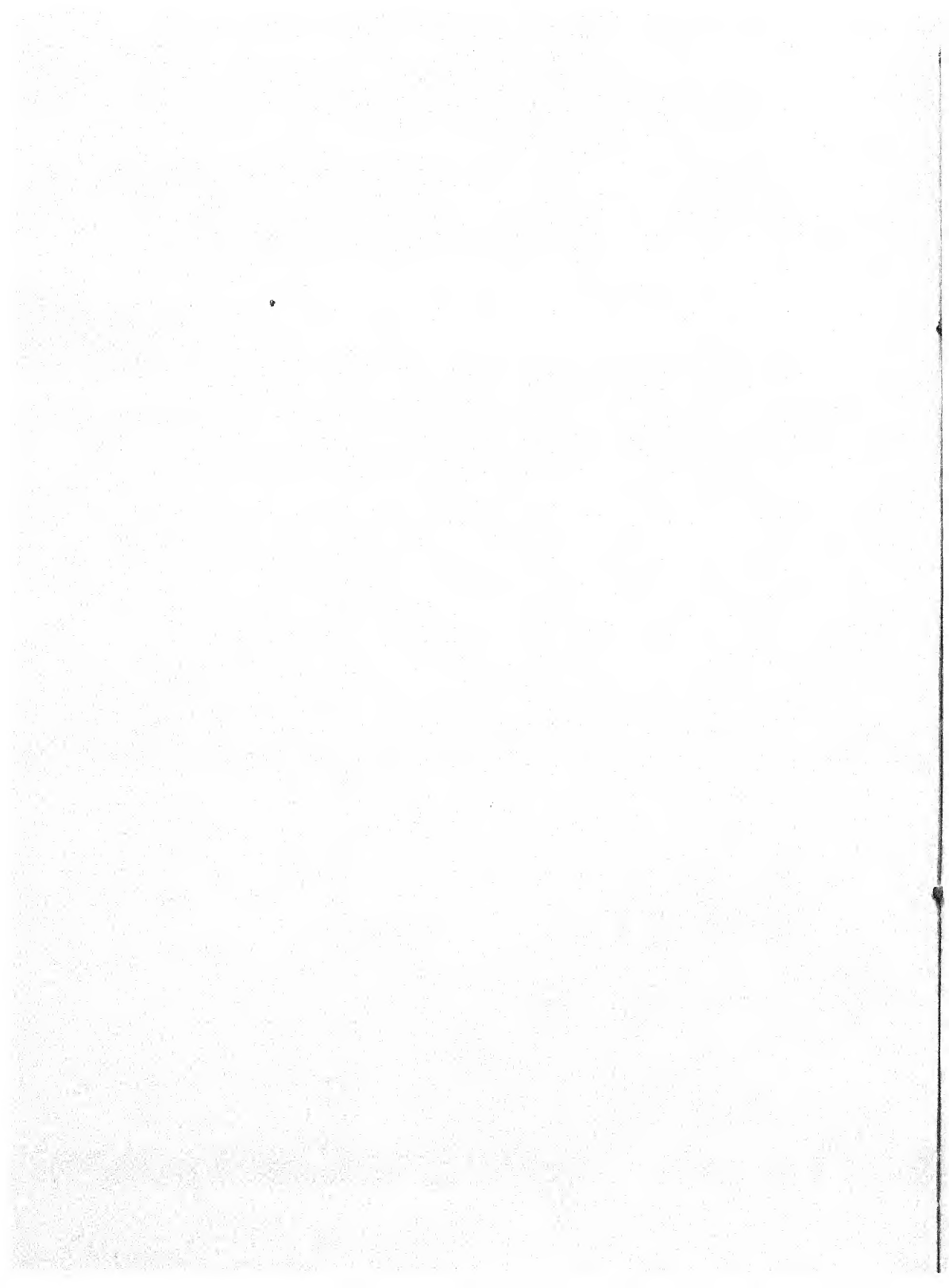
The Davidson soil profile displays a partially podzolized A horizon, with slight accumulation of iron oxide in the B₂ horizon. Humid tropical red earth profiles usually display similar but much more pronounced differentiation; their A horizon in some instances consists almost entirely of residual quartz sand.

In order fully to trace the mineralogical and chemical transformations that occur during the genesis of red earths from basic igneous rocks, and to elucidate the processes involved in laterization and podzolization, the application of modified and additional methods of silicate analysis is urged, as well as the employment of dye tests, microscopical examination, and other simple laboratory methods. It is insufficient merely to determine the component oxides constituting rock-weathering products and soil profile horizons; differentiation should be made between those oxides which occur in the free (often hydrous) state and those which are combined.

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FACTORIAL DIAGRAMS

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The term *factorial diagram* may denote a diagram of data resulting from some experiment with factorial design. Such data, which may be denoted as *factorial data* and which are measurements of some property, can be considered as a variable, depending on the factors as independent variables. Analytically, factorial data, as dependent on their factors, can be considered as a polydimensional system. The order of dimension equals the number of factors plus one. For a single factor such a system can be represented diagrammatically by a line in a flat plane. For two factors the straightforward diagram would be a three-dimensional structure in space, whereas for more than two factors the corresponding diagrams would be imaginary. For two and three factors special indirect diagrams have been proposed, but these will not be discussed here.

The author has used in his work for many years a method of indirect diagrams in a flat plane which is applicable to any number of factors. As this method may be useful to other experimental workers, it is described in this paper.

The method is illustrated by a field experiment with tapioca (*Manihot utilissima* Pohl) laid out on the north coast of West-Java in a red volcanic clay loam, which was known to be very deficient in potassium, appreciably less so in phosphorus, and much less so in nitrogen. The chief purpose of the experiment was to test the availability of the soil phosphorus. This point will not be considered further, as it is irrelevant to the present purpose. The data obtained for fresh-tuber weights and for dry-starch weights are utilized here for explaining the diagrammatical method under consideration.

The experiment, T.503 (the author's register number), was of straightforward factorial design with 3 potassium, 3 phosphorus, and 4 nitrogen levels, including for each factor a 0 level. The 36 treatments were not replicated, as the area of land of the quality desired was only just large enough for 36 minimum-sized plots. The 36 plots were randomized over the whole experimental area, i.e., without confounding. Table 1 gives the necessary information on the levels and on the forms and quantities of fertilizer applied. The levels are denoted in two ways; for example, the 1st nitrogen level can also be spoken of as the 0 level for nitrogen; the 2nd phosphorus level, as the single-phosphorus level; the 3rd nitrogen level, as the double-nitrogen level.

In this table the treatments are denoted each by three numbers, which denote by their *position* from left to right the factors: potassium, phosphorus, and nitrogen. This, and not the usual NPK sequence, has been chosen in correspondence with this particular sequence of the factors in the diagrams, as produced in this paper. The numbers themselves denote the relative levels of each of the factors: thus, 024 means the combination of the double-phosphorus level with the quadruple-nitrogen level in the absence of potassium.

Diagram 1 is that for the tuber yields. The diagram consists of 36 points, corresponding to the 36 treatment yields. The unit of ordinates is equal for all the yields, and the origin is identical for all the ordinates. Thus the yields are measured by their vertical distance from the axis of abscissas.

Matters are different regarding the abscissas. It will be seen in diagram 1 that between the yield points three different sorts of lines have been drawn; viz., 1 dotted line, 3 broken lines, and 9 full lines, corresponding with the potassium line, 3 phosphorus lines, and 9 nitrogen lines. From the yield

TABLE 1
Forms and quantities of fertilizer applied in experiment T.503

FERTILIZERS	POTASSIUM, IN FORM OF SULFATE OF POTASSIUM CONTAINING 90 PER CENT SULFATE			PHOSPHORUS, IN FORM OF DOUBLE SUPERPHOSPHATE CONTAINING 36 PER CENT P ₂ O ₅			NITROGEN, IN FORM OF SULFATE OF AMMONIA CONTAINING 21 PER CENT N			
Levels	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	4th
Relative-level de- notation	0	1	2	0	1	2	0	1	2	4
Quantities of the forms per plant*	0	36	72	0	12	24	0	12	24	48

* The plants were spaced 3 by 3 feet.

point as in the axis of ordinates, i.e., the yield point of the 000 treatment, in short from the 000 point, originate the potassium line, the 1st phosphorus line, and the 1st nitrogen line. These three lines are ordinary yield diagrams for one factor in a flat plane, or regression lines of yield on the particular single-factor concerned. The formulas for these lines, which will easily be understood without further explanation, are: 000-100-200, 000-010-020, and 000-001-002-004.

Whereas for these three regression lines the unit of ordinates is identical, their units of abscissas, i.e., the abscissas for the single levels of the factors, are different for the different factors. The choice of these units is, in general, arbitrary, but to assure as little as possible intersecting of lines in the diagram, the units have been chosen thus: 1 nitrogen line equals 4 units of nitrogen abscissas, 1 unit of phosphorus abscissas equals 4 + 1 or 5 units of nitrogen abscissas, and 1 unit of potassium abscissas equals 5 + 5 + 4 + 1 or 15 units of nitrogen abscissas. Thus equal apparent-regressions for nitrogen, phosphorus, and potassium in the diagram correspond to real regressions,

which are in the ratio of $1/15$ to $1/5$ to 1 . Within all the nitrogen lines, however, regressions are on an identical scale, and so within all the phosphorus lines; there is, of course, also only one scale of regression within the one potassium line.

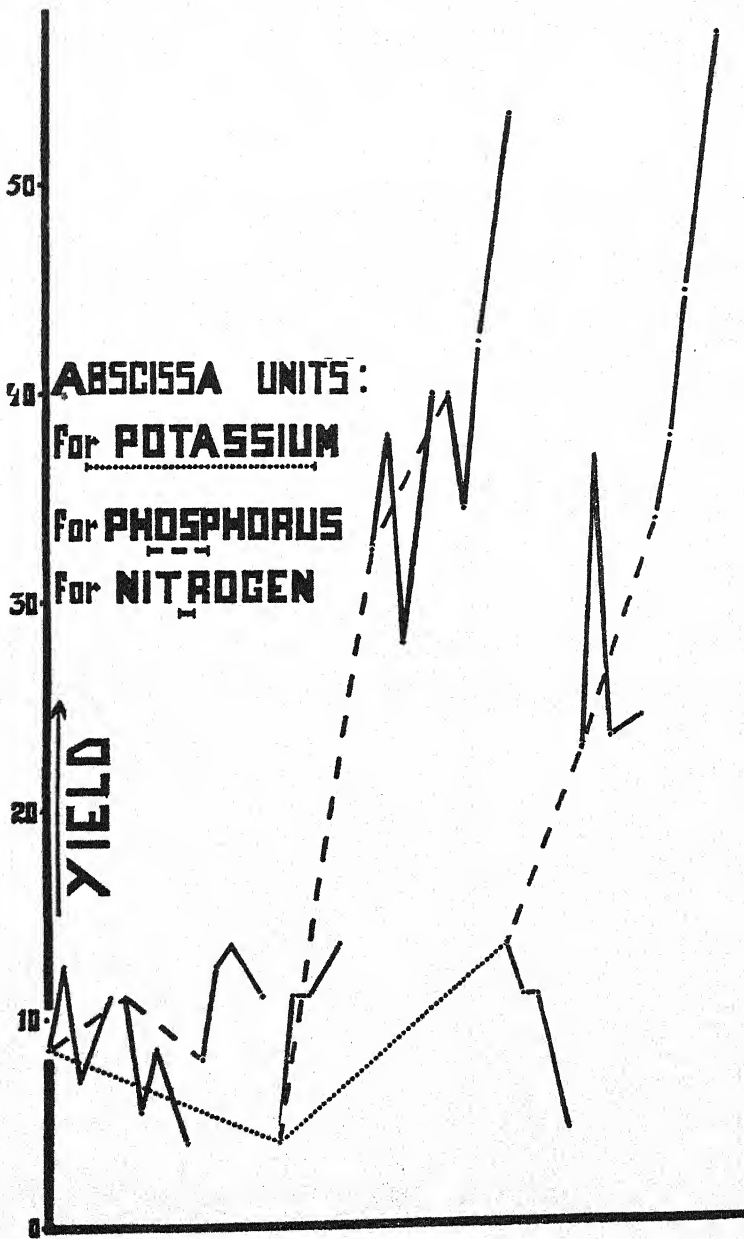


DIAGRAM 1. YIELD OF FRESH TAPIOCA ROOTS, IN TONS PER HECTARE, WITH DIFFERENT FERTILIZER TREATMENTS IN EXPERIMENT T.503

In diagram 1 will be noticed, besides the potassium line, the 1st phosphorus line, and the 1st nitrogen line, 2 further phosphorus lines, and 8 further nitrogen lines. Whereas the first 3 lines have an identical origin, all the other 10 lines have different origins. The formulas for the first 3 lines have already been given; those for the other 10 can easily be derived. For the 2nd phosphorus line, originating from the 100 point of the potassium line, for example, the formula can formally be derived from that of the 1st phosphorus line by adding to each member of the latter the numerical value of the point of origin of the former, as follows:

Formula of	1st phosphorus line =	000 - 010 - 020
Formula of origin of 2nd phosphorus line =	100 =	100 = 100
Formula of	2nd phosphorus line =	100 - 110 - 120

In table 2 the derivations of all the lines of diagram 1 are to be found. As one nitrogen line contains 4 yield points, all the 9 nitrogen lines contain 36 yield points, i.e., all the yield points of the diagram. Thus in table 2 all the data on starch-yields and costs can be found after the formulas of the nitrogen lines. Some of these data are repeated after the formulas of the potassium and phosphorus lines, with a view to including in table 2 also for these lines the yield data in the sequence of their formulas.

With the aid of table 2 it is very simple to draw diagram 1. After having fixed the units of abscissas for the three factors, the potassium line, the 1st phosphorus line, and the 1st nitrogen line are drawn, the yield values for which are to be found in the correct order after their formulas in table 2. With the exception of their common origin, every yield point of these three lines is a point of origin for another nitrogen line, the yield data for which are also to be found in their correct order in table 2.

Graphically the three factors take a differential position in diagram 1, with the result that there is only one single line for potassium and that there are 3 lines for phosphorus and 9 for nitrogen. The position assigned to potassium may be denoted as the primary, that of phosphorus the secondary, and that for nitrogen the tertiary. If the primary position remains assigned to potassium but the positions for the other two factors are interchanged, the corresponding diagram will consist of 1 potassium line, 3 nitrogen lines, and 9 phosphorus lines. As the primary position can be assigned to every one of the three factors and in each case the other two factors can be interchanged, 6 diagrams can be constructed for one set of factorial data with three factors. In each of these 6 cases the line formulas can be found by interchanging in the appropriate way the places of the three factors in the first column of table 2 and by interchanging correspondingly the treatment formulas in the second column. It is evident that every one of the 6 possible diagrams contains the identical amount of information as every other of the 6. According to the author's experience, it seems best to assign the positions to the various factors in order

TABLE 2
Yields of fresh tubers and dry starch in experiment T. 503 and corresponding formulas for treatments and regression lines

REGRESSION LINES		FORMAL DERIVATIONS OF FORMULAS FOR REGRESSION LINES	TREATMENT FORMULAS, ARRANGED IN ORDER OF FORMULAS FOR REGRESSION LINES	FRESH-TUBER YIELDS, IN TONS PER HA., ARRANGED IN ORDER OF REGRESSION LINES	DRY-STARCH YIELDS, IN TONS PER HA., ARRANGED IN ORDER OF REGRESSION LINES	COSTS OF FERTILIZING,* IN D.E.L. F PER HA., ARRANGED IN ORDER OF REGRESSION LINES
Potassium line			000-100-200	8.5- 4.0-13.5	2.63- 1.18- 4.16	0- 41- 80
1st	Phosphorus line	(000-010-020) + 000	000-010-020	8.5-11.0- 8.0	2.63- 3.14- 2.19	0- 15- 28
2nd		(000-010-020) + 100	100-110-120	4.0-32.5-40.0	1.18-10.28-12.23	41- 54- 67
3rd		(000-010-020) + 200	200-210-220	13.5-23.0-34.0	4.16- 6.73-10.92	80- 93-106
1st	Nitrogen line	(000-001-002-004) + 000	000-001-002-004	8.5-12.5- 7.0-11.0	2.63- 3.94- 2.23- 3.51	0- 12- 23- 44
2nd		(000-001-002-004) + 010	010-011-012-014	11.0- 5.5- 8.7- 4.0	3.14- 1.45- 2.32- 1.01	15- 25- 36- 58
3rd		(000-001-002-004) + 020	020-021-022-024	8.0-12.5-13.5-11.0	2.19- 3.55- 4.20- 3.47	28- 39- 49- 71
4th	Nitrogen line	(000-001-002-004) + 100	100-101-102-104	4.0-11.0-11.0-13.5	1.18- 3.46- 3.57- 4.20	41- 51- 62- 84
5th		(000-001-002-004) + 110	110-111-112-114	32.5-38.0-28.0-40.0	10.28-12.19- 9.45-12.59	54- 65- 75- 97
6th		(000-001-002-004) + 120	120-121-122-124	40.0-34.5-42.5-53.0	12.23-10.90-13.97-16.91	67- 78- 88-110
7th	Nitrogen line	(000-001-002-004) + 200	200-201-202-204	13.5-11.0-11.0- 4.5	4.16- 3.20- 3.50- 1.33	80- 90-101-123
8th		(000-001-002-004) + 210	210-211-212-214	23.0-37.0-23.5-24.5	6.73-10.86- 7.22- 7.29	93-104-114-136
9th		(000-001-002-004) + 220	220-221-222-224	34.0-38.0-45.0-57.5	10.92-11.13-13.80-17.91	106-117-127-149

* As at time of fertilizing, when \$1 = f 1.82; including costs of application.

of descending importance as regards their experimental effect, the primary position being assigned to the factor with the most important effect.

As has been mentioned, in general the choice of the units of abscissas is arbitrary. In diagram 1 the choice has been limited by the practical consideration of obtaining as little intersecting of lines as possible. As has also been explained, in diagram 1 regression is not intercomparable for the different sorts of lines but it is intercomparable within equal sorts of lines. If it is desired to make all the regressions within the whole diagram intercomparable, all the factors should be measured in a single unit and the units of abscissas should be chosen equal for all the factors. Thus, for example, in a water-culture experiment all the food factors might be expressed in terms of osmotic pressure of the factor ions in the culture solution. This may lead to a very important diagram from a physiologic point of view, although much intersecting of lines might thus become a hindrance to the visual effect of the diagram.

In the present field experiment with tapioca, a common unit of abscissas for the three factors is found in the monetary costs of fertilizing. The varying costs per treatment then become the abscissas for the corresponding treatment yields. These costs of fertilizing are to be found in the last column of table 2, and in diagram 2 they have been used as abscissas for the corresponding starch yields, which are to be found in the fifth column of table 2. In diagram 2 the starch yields are measured by their vertical distance from the axis of abscissas, whereas the corresponding costs of fertilizing are measured by their vertical distance from the axis of ordinates.

In diagram 2 a few straight lines have been drawn with the 000 yield-point as the common origin. For every point of such a line the vertical distance from the axis of ordinates measures costs of fertilizing, producing a yield increase of starch, as measured by its perpendicular distance from the 000 point. The quotient of such a cost figure with its corresponding yield figure represents the costs, producing a yield increase of 1 ton of starch. As these quotients are constant within each such line, the points of intersection of such a line with the diagram lines indicate factor combinations for which costs per ton of starch-yield increase are equal to those of all the points of the intersecting line. In diagram 2, such lines, as originating from the 000 point have been drawn for f 5, f 7.50, and f 10 per ton of starch-yield increase. It will readily be seen that diagrams such as diagram 2 may be very important tools in estate practice.

Finally, an example may be given of how factorial diagrams can assist visually in understanding the interrelations between factorial data.

In diagram 1 it is visually clear that a distinction should be made between a low-yield group and a high-yield group, the upper limit for the low-yield group being about 14 tons of tubers per hectare. Furthermore, considering the fact that the treatments have not been replicated, it is equally clear that no statistical significance can be assigned to the differences within the low-yield group. Also it will scarcely need calculation to find a significant difference between the two groups.

It is visually apparent that tuber yield can disengage itself from the low-yield group only if the phosphorus and potassium fertilizer treatments are

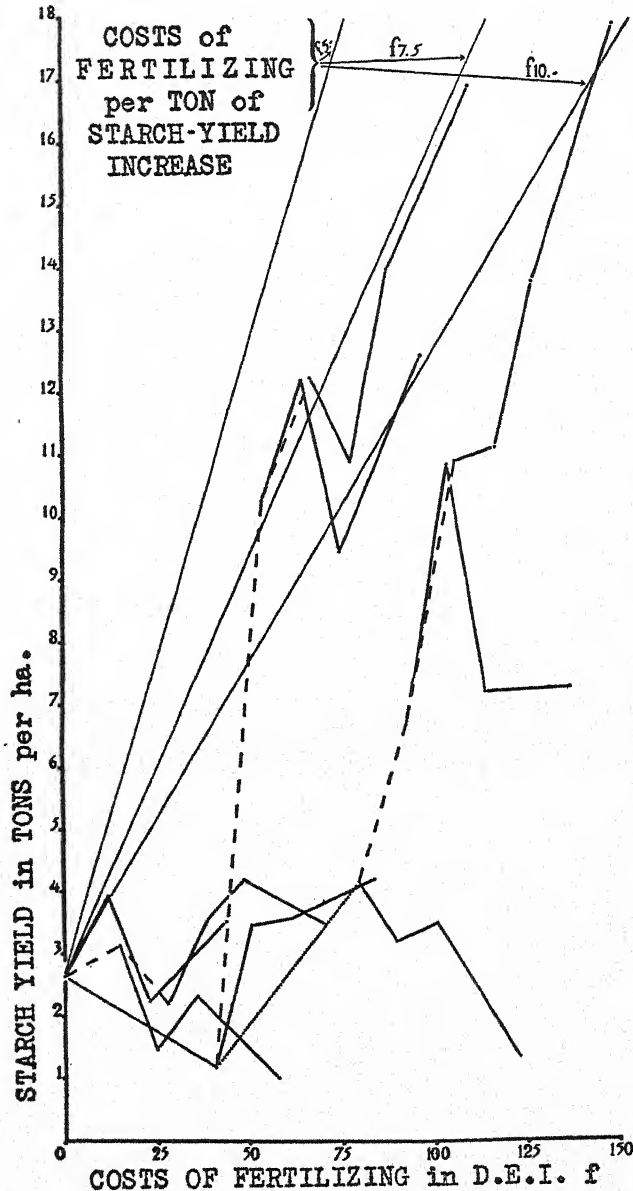


DIAGRAM 2. COSTS OF FERTILIZING AND STARCH YIELDS IN EXPERIMENT T.503

combined. Potassium alone or phosphorus alone, either with or without nitrogen, causes either no or only a statistically insignificant yield increase or

yield depression. It may thus be inferred that either potassium or phosphorus was only just sufficiently available in the soil of experiment T.503 to feed the tapioca for the 000 yield, whereas the other of these two factors, as far as available, could sustain no higher yield or only a statistically nonsignificant higher yield. Nitrogen, however, must have been comparatively much more abundant than either potassium or phosphorus in the soil of the experiment, because without nitrogen large yield increases could be obtained by fertilizing with combinations of potassium and phosphorus.

The 2nd and 3rd phosphorus lines may now be considered as distinct from their dependent nitrogen lines. From the course of the 2nd phosphorus line it is apparent that the single potassium level, combined with the single phosphorus level, gives a large yield increase, and that a further phosphorus addition to such treatment adds little more to the yield effect. The inference from this is that by potassium and phosphorus additions, as in the 120 treatment to the soil of T.503, the ratio of available potassium to available phosphorus in this soil remains or becomes nearly optimal for tapioca-tuber yield. A deduction from this inference is that a potassium addition to the 120 treatment should, by its unbalancing effect on the ratio, depress the 120 yield. Indeed, it is readily seen in diagram 2 that the 220 yield is lower than the 120 yield, the difference being 6 tons per hectare. A further deduction is that the unbalancing effect of the addition of one potassium unit would be larger if the phosphorus level in the treatment were lower. Indeed, diagram 2 shows that the depressing effect of one potassium unit added to the 110 treatment is much larger than that of a similar unit added to the 120 treatment, viz., 9.5 as against 6 tons per hectare.

This may suffice to show the importance of the visual assistance of factorial diagrams in interpreting the interrelations between factorial data.

PHYSICAL CHARACTERISTICS OF SOILS: V. THE CAPILLARY TUBE HYPOTHESIS OF SOIL MOISTURE

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The simple concept of the soil as a bundle of capillary tubes to which the laws of surface tension and capillarity could be applied, was one of the earliest attempts to explain soil moisture distribution. What may, therefore, be called the "capillary tube" hypothesis found an early place in the literature. Keen in his review of the subject has rejected the hypothesis (2) mainly on the ground that experimental evidence in support of it has been lacking. The upward capillary movement in soils is effective only to a limited distance, and the theoretical value is by no means approached in actual practice. Even the lowest of these estimates is in excess of the experimental values with tubes of soils, where 4 or 5 feet is seldom reached. The present paper presents experimental evidence in support of the contention that the capillary tube hypothesis is essentially sound and that only defective experimental technic has prevented us so far from realizing in practice the values demanded by theory.

The well-known formula for the height to which water rises in a vertical capillary tube which is wetted by water and the lower end of which is in water is

$$h = \frac{4T}{g\sigma d} \quad (A)$$

where h = height of meniscus above water level, T = surface tension of water in air, g = acceleration of gravity, σ = density of water, and d = diameter of the capillary tube. Substituting the numerical values (C.G.S. system) in equation (A) we have approximately

$$h = \frac{0.30}{d} \quad (B)$$

In applying this equation to the rise of water in soil, d must be regarded as the equivalent diameter of a capillary tube made up of the spaces between the particles. The relation between d and the diameter of the particles D has been worked out by Slichter in the case of an ideal soil, i.e., one having particles of the same diameter (9). His analysis shows that the value of d at the widest part of the triangular pores between the particles is $0.288 D$ where D

is the diameter of the spheres in the ideal soil. Equation (B) therefore could be written as:

$$h = \frac{0.30}{0.288D} = \frac{1}{D} \text{ approximately} \quad (C)$$

In other words, the height of capillary rise is approximately equal to the reciprocal of the diameter of the particles, both quantities being expressed in the same unit.

The capillary theory demands that the soil should be saturated with water at all points between the water table and the upper limit of capillary rise. No serious attempt has been made, however, to ensure this condition in the experiments devised for measuring the upper limit of capillary rise of water in soils. As a matter of fact, any measurement of the capillary force of soil particles obtained by allowing this force to raise water is fundamentally wrong, as it is impossible to dislodge air. Such a procedure is only applicable in a single tube. The futility of such an attempt can be readily realized by trying to fill a sintered glass Büchner funnel completely by forcing water from below. The only logical method of studying the capillary phenomenon in soils is to start from the state of saturation when the capillaries are completely full of water.

EXPERIMENTAL

The apparatus for measuring capillarity, shown in figure 1, is essentially similar to the one used by Haines (1). The ordinary porcelain Büchner funnel used by Haines has been replaced by a sintered glass one, and the pressure deficiency is applied by sliding a burette tube against a graduated scale. The funnel is filled with water by inserting a rubber bung at the top, inverting it, and joining it to the rubber tube leading to the burette. The connecting rubber tube is kept full of water when being joined to the Büchner funnel, and if the burette tap is kept slightly open the flow of water ensures an air-free joint. It is essential that no air be allowed to remain at the lower surface of the filtering disk. Excess of water is removed from the funnel and is replaced by a quantity of sand to give a layer about one-half centimeter thick with some free water standing on top.

At the start, the level of water on top of the sand and in the burette tube is the same. The burette tube is lowered in steps of 1 cm. or so, and the rise of water is noted in terms of the graduations on the tube. This continues until the free water surface over the sand disappears and the capillary pull of the water held in the interstices comes into play. From this point onward, further lowering of the burette tube causes no rise in the level of the water contained in it. This constant value continues until the difference of pressure exceeds the capillary pull of the sand and the water again begins to rise in the burette tube. There is a definite break if the layer of sand is only a few millimeters thick. On the other hand, if the sand layer is a few centimeters thick, the

capillary front recedes as the burette tube is lowered, and some water is yielded at every step. This point will be referred to again.

The water levels in the burette are plotted against the scale readings, and the vertical portion of the curve represents the capillary pull (fig. 2, curve I). When the sand is very coarse and its thickness is over 1 cm., a slight bend is observed in the curve just before the break point (fig. 2, curve II). This is due to the fact that the surface of coarse sand is uneven and some water is held

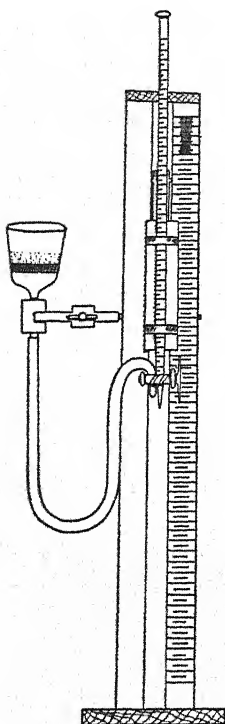


FIG. 1

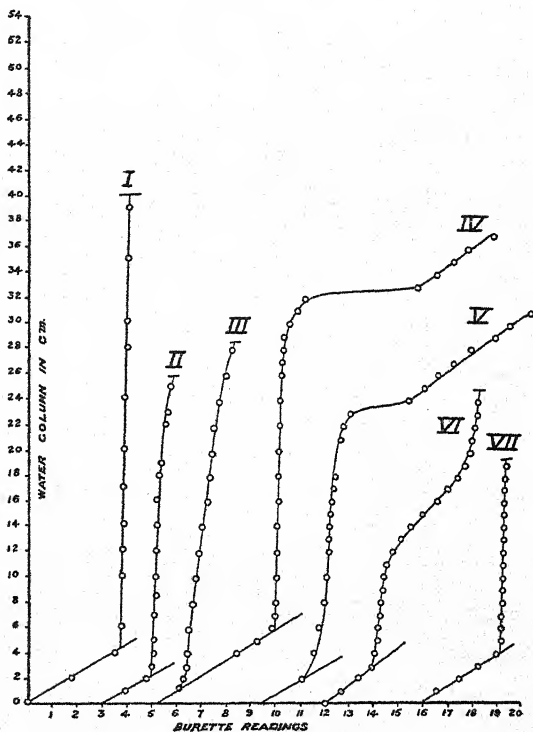


FIG. 2

FIG. 1. APPARATUS FOR MEASURING CAPILLARY FORCE OF AGGREGATES

FIG. 2. DIFFERENT TYPES OF CURVES ILLUSTRATING CAPILLARY FORCE OF AGGREGATES
Ordinate of curve III, Hg column in cm.

in the corner where the sand touches the walls of the Büchner funnel. This water, therefore, is yielded when the capillaries recede in the inside. This corner effect is also pronounced when the sand layer is a few centimeters thick, and the break is followed by another line which is due to the receding capillary front (fig. 2, curves IV and V). It might be pointed out that the introduction of this complication is unnecessary, as a definite break can always be obtained by keeping the layer of sand only a few millimeters thick.

It must be emphasized that there is a limit to the application of pressure deficiency in this particular way, which extends only up to the point that the

capillaries remain *completely* full. The moment the continuity of capillary water is broken and air has entered, the pressure deficiency as applied by lowering the water column has no meaning. Haines failed to recognize this point and carried his pressure deficiency beyond the stage of air entry, i.e., when the capillaries were only partly full. His purpose was to demonstrate the three stages of moisture which he recognized, following Versluys' nomenclature; namely, the *pendular*, the *funicular*, and the *capillary*. It is only in the last stage that the capillaries are supposed to be full and it is only this stage that can be measured with an apparatus of this kind. Any attempt to increase the pressure deficiency beyond this stage can only result in a rupture of the capillaries, and transmission of pressure is rendered impossible. The so-called hysteresis loops obtained by Haines were also due to air spaces which are bound to remain in a moist sand when water is pushed into it from below. It is worthy of note that the filter paper or the sintered glass filtering disk has a capillary pull (fig. 2, curve VII), and if this is greater than that of the sand above, no definite break is observed, in the first instance, because the receding capillaries are again held by the filter paper (fig. 2, curve VI). The capillary pull of the latter, therefore, should always be lower than that of the sand under examination.

With the help of the capillarimeter described, we can measure the maximum capillary force that can develop in a sand or soil and therefore test the relation between the diameter of particles and maximum capillary force. For this purpose, 107 sands and 11 soils were examined. Of the sands, 26 were of uniform diameter and had been separated by the author's siltometer (3) to conform as closely as possible to the diameters given. Others were natural sands obtained from canal beds and were of widely varying origin. The mean diameters of these sands were determined from their distribution curves in the manner described elsewhere (6). These values are compared to the values obtained by the capillarimeter from the relation $h = \frac{1}{D}$ where h is the maximum

capillary pull and D is the mean diameter of particles. It will be seen from table 1 A-C that the agreement between the two sets of values is as good as could be expected, and would leave no doubt as to the soundness of the capillary hypothesis, especially as the range of diameters studied is from 0.02 to 4 mm. Alternately the capillarimeter could be used for measuring the mean diameter of sands and soils, and thus is expected to be helpful in studying the regimes of canals which are influenced by the grade of the silt that is passing.

The results with soils need special mention. The clay content of the soils varied from 11.5 to 68.2 per cent, and the mean diameter refers to their distribution curves obtained at maximum dispersion as well as without dispersion. The maximum capillary force actually determined lies somewhere between the calculated values for mean diameter at maximum dispersion and without dispersion (table 1 C). This is what one would expect in view of the uncertainty regarding the state of aggregation of a wet soil. It might be noted that par-

TABLE 1 A
Calculated and found values of capillary columns—natural silts

	MEAN DIAMETER	CAPILLARY COLUMN			MEAN DIAMETER	CAPILLARY COLUMN	
		Determined	Calculated			Determined	Calculated
	mm.	cm.	cm.		mm.	cm.	cm.
1	.512	19.8	19.5	42	.181	54.7	55.2
2	.501	20.0	20.0	43	.230	35.6	43.5
3	.493	18.9	20.3	44	.205	49.0	48.8
4	.483	19.8	20.7	45	.189	44.0	52.9
5	.476	21.0	21.0	46	.226	43.5	44.2
6	.467	20.6	21.4	47	.126	83.5	79.4
7	.441	23.4	22.7	48	.129	47.4	77.5
8	.432	22.1	23.1	49	.131	78.0	76.3
9	.403	25.5	24.8	50	.136	67.6	73.5
10	.388	26.8	25.8	51	.151	69.0	66.2
11	.389	28.4	25.7	52	.172	57.2	58.1
12	.345	29.6	29.0	53	.178	59.2	56.2
13	.338	31.6	29.6	54	.208	51.6	48.1
14	.325	33.2	30.8	55	.197	61.7	50.8
15	.320	33.0	31.3	56	.202	46.3	49.5
16	.288	41.3	34.7	57	.159	67.4	62.9
17	.255	49.0	39.2	58	.250	41.2	40.0
18	.381	28.0	26.2	59	.133	79.7	75.2
19	.355	26.5	28.2	60	.204	50.6	49.0
20	.278	36.2	36.0	61	.340	29.3	29.4
21	.274	38.0	36.5	62	.363	30.5	27.5
22	.274	36.0	36.5	63	.369	29.3	27.1
23	.330	32.7	30.3	64	.313	32.2	31.9
24	.353	32.0	28.3	65	.242	44.7	41.3
25	.711	17.5	14.1	66	.205	45.0	48.8
26	.646	21.4	15.5	67	.306	35.7	32.7
27	.636	17.8	15.7	68	.225	42.1	44.4
28	.624	17.6	16.0	69	.227	43.7	44.1
29	.231	44.4	43.3	70	.269	34.0	37.2
30	.332	31.3	30.1	71	.356	27.2	28.1
31	.227	41.4	44.1	72	.215	48.0	46.5
32	.141	66.4	70.9	73	.201	43.5	49.8
33	.117	94.3	85.5	74	.261	40.5	38.3
34	.166	56.9	60.2	75	.245	37.7	40.8
35	.185	55.5	54.1	76	.250	40.8	40.0
36	.188	55.3	53.2	77	.283	35.0	35.3
37	.201	52.5	49.8	78	.351	28.8	28.5
38	.216	46.4	46.3	79	.263	39.0	38.0
39	.179	64.3	55.9	80	.338	28.8	29.6
40	.223	47.1	44.8	81	.332	24.7	30.1
41	.147	42.7	68.0				

ticles having diameters of 0.02 cm. or more settle quickly to the bottom of the funnel, and the remaining soil behaves as if it were devoid of these particles. In calculating the mean diameters of the soils, the portion of the distribution

curve above 0.02 cm. diameter is not taken into consideration, and the results are calculated as if these particles were absent. Another point worthy of note is that soils should be soaked in water for 24 hours before their capillarity is measured. A layer of fine sand is spread on the sintered funnel with some free water at the top. Dry soil is gradually added on top of the sand layer and allowed to soak in the water for 24 hours. After this the capillary force is

TABLE 1 B
Calculated and found values of capillary columns—silt and sand fractions

	MEAN DIAMETER	CAPILLARY COLUMN	
		Determined	Calculated
	mm.	cm.	cm.
1	3.0 -4.0	3.5	2.9
2	2.0 -3.0	5.4	4.0
3	1.3 -2.0	6.3	6.1
4	1.0 -1.3	8.8	8.7
5	0.88 -1.0	13.0	10.6
6	0.6	14.4	16.7
7	.56 - .60	23.2	17.24
8	.49 - .56	24.4	19.0
9	.44 - .49	27.4	21.5
10	.40 - .44	26.6	23.8
11	.36 - .40	29.7	26.3
12	.34 - .36	30.6	28.6
13	.31 - .34	32.8	30.8
14	.29 - .31	36.3	33.3
15	.28 - .29	36.3	35.1
16	.26 - .28	37.8	37.0
17	.25 - .26	36.7	39.2
18	.22 - .25	41.1	42.6
19	.20 - .22	44.9	47.6
20	.19 - .20	46.0	51.3
21	.17 - .19	50.4	55.6
22	.15 - .17	55.9	62.5
23	.13 - .15	69.1	71.4
24	.12 - .13	77.0	80.0
25	.08 - .12	90.6	100.0
26	.065- .08	94.1	137.9
Lead shots			
1	1.32 -1.5	6.8	7.1
2	1.0 -1.32	7.9	8.6

measured as usual. The part of the curve after the capillarity comes into operation and the free water surface has disappeared, is not vertical (fig. 2, curve III). Unlike sands, soils yield some water at every increase of pressure deficiency. There is also a corresponding decrease in the volume of the soil as the water is squeezed out and the particles come closer and closer. This phenomenon is entirely due to the swelling of soil colloids and is not funda-

mentally related to the moisture content and pressure deficiency. Increasing deviations from the vertical simply indicate increasing amounts of colloids. The point will be referred to again. As equilibrium is also reached at a much slower rate in soils than in sands, at least 15 minutes are allowed between successive readings. While studying the capillary force of soils, it is not convenient to work with water columns 3 or 4 m. long. The burette tube and a part of the connecting tube is filled with mercury, therefore, and the pressure deficiency is applied by lowering the mercury column, which can be converted into terms of the height of water column, if required. In table 1 C, the calculated and found values of capillary pull of soils are given in terms of the mercury column.

TABLE 1 C
Calculated and found values of capillary columns—soils

SOIL NUMBER	CLAY (.002 mm.)	MEAN DIAMETER*		CAPILLARY COLUMN†		
		Dispersed	Undispersed	Determined	Calculated	
					Dispersed	Undispersed
	<i>per cent</i>	<i>mm.</i>	<i>mm.</i>	<i>cm.</i>	<i>cm.</i>	<i>cm.</i>
P.C. 1	11.50	.0246	.0373	22.80	30.00	19.79
2	64.06	.0229	.0730	18.8	32.23	10.11
3	68.21	.0233	.0737	21.3	31.67	10.01
4	15.56	.0329	.0499	24.4	22.43	14.79
5	12.79	.0342	.0475	18.5	21.58	18.54
6	29.73	.0326	.0642	19.0	22.64	11.50
8	27.30	.0497	.0789	17.4	14.85	9.35
9	22.90	.0493	.0863	9.0	14.97	8.55
10	38.62	.0394	.0845	21.0	18.73	8.73
11	35.08	.0435	.0980	16.0	16.97	7.53

* Excluding particles over 0.2 mm.

† Height of mercury.

It has already been pointed out that if the sand column is long, there is no break, but a sharp bend through the vertical part of the capillary curve corresponds to the maximum capillary pull. An important question arises in this connection as to what might be the moisture gradient in a sand column with the receding capillary front. It is also important to know whether the moisture content of the sand column above the capillary front is influenced by the extent to which the latter has been lowered. In other words can the receding capillary front draw down some moisture from the top or has the sand column above the capillary front no connection with it, so that it could be removed without affecting the state of equilibrium of the lower part. A column of sand 100 cm. long was made by filling with sand glass tubes 2.2 cm. in diameter and 10 cm. long, joined with rubber tubing, taking care that all the air was displaced and there was free water at the surface. The tube was then allowed to drain, by gradually lowering the water reservoir.

After 24 hours, during which the top of the tube was protected from evaporation, the glass sections were separated by slitting the rubber joints vertically and making a clean cut by running a wire across the sand column. The various sections were immediately transferred to lead moisture tubes (7), and moisture content was determined by evaporating to dryness at 100–110°C. The results are plotted in figure 3. It will be seen that there is an abrupt change in the moisture content. The smoothness of the curve drawn through the midpoints is only indicative of the fact that the receding capillary front is not a sharp line. Actually the difference between its lowest and its highest points may be 5 or 6 cm. An absolutely sharp rise cannot be expected in view of the fact that the sections were chosen at regular intervals from the top and not from the capillary front, which was almost in the middle of one of the sections.

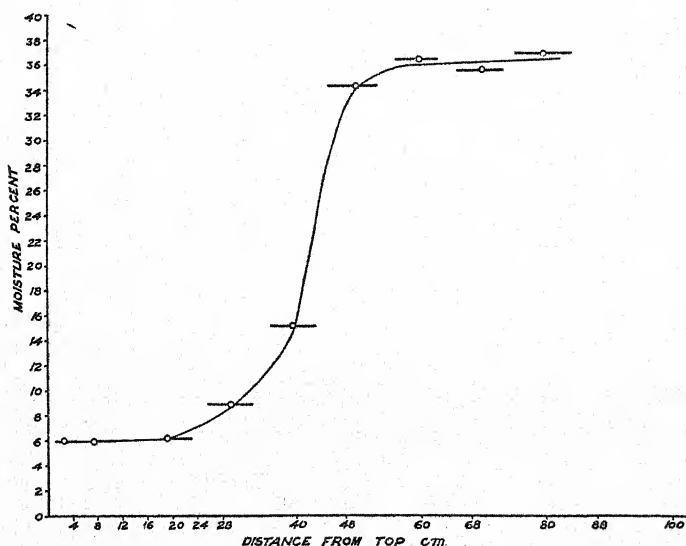


FIG. 3. MOISTURE DISTRIBUTION IN A SAND COLUMN UNDER A RECEDING CAPILLARY FRONT

The results leave no doubt, however, that in the capillary phenomenon, the capillaries are either full or empty. It is important to note that there is no connection between the top part at 6 per cent moisture and the lower part at 35 per cent moisture except through stray capillary tubes of short length just above the receding capillary front. The removal of the upper glass sections had no influence on the lower ones, which remained at the same moisture content, and the connecting burette tube showed no change in reading.

In order to determine whether the residual moisture content of the sand, when the capillaries have emptied, is characteristic of the particle size, a number of sands were examined in a similar way by applying pressure deficiency until the capillary front had receded far down. The results, plotted in figure 4, show that there is a correlation between the size of the particles (D) in milli-

meters and the residual moisture percentage (M). This relation may be expressed by the formula:

$$M = \frac{1.65}{D}$$

No special significance seems to attach to the value 1.65 in this formula, beyond the fact that the moisture content would reach a very high value when the diameter of the particles was less than 0.1 mm. In soils with an average diameter of the order of 0.02 mm. the corresponding moisture contents would assume ridiculously high values. The limited applicability of the formula therefore should be recognized. It appears, however, that as the particle size becomes smaller, the difference between the moisture content when the capillaries are full and the residual moisture, narrows and in extreme cases might become negligible.

Schofield has endeavored to express the moisture content of soils in terms of free energy relationship (8). If we suppose that water is held by soil against

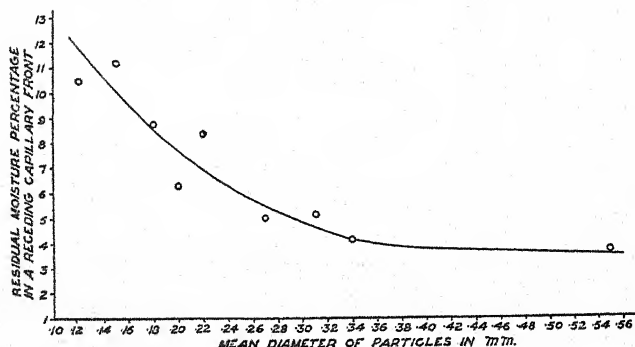


FIG. 4. RELATION BETWEEN PARTICLE SIZE AND RESIDUAL MOISTURE IN A RECEDING CAPILLARY FRONT

a suction force tending to displace it, the free energy can be expressed in terms of the height in centimeters of the equivalent water column. In order to deal conveniently with the whole range of suction, use is made of the logarithm of this height. By analogy with Sørensen's logarithmic acidity scale, the symbol pF has been used (F being the recognized symbol for free energy). From equation (C) we can express the relation between the diameter D of particles and its pF as:

$$pF = -\log D \quad (D)$$

We can, therefore, express the summation curves of soils in terms of free energy, or pF . Such curves, of course, will not be different from the ordinary summation curves on the semilogarithmic scale, but they will bring out more clearly the fact that in soils we have particles of a diameter which can form capillaries

of the order demanded by theory. Summation values and other relevant data for two soils are given in table 2. Particles up to the diameters corresponding to pF 5.03 were determined by the pipette method; values for pF 6 are extrapolated from the summation curves. It is admitted that not much reliance can be placed in the extrapolated values on a logarithmic scale, but there is no mistaking the general trend of the extrapolated portion. These soils are of unusual interest, because in spite of the fact that P.C. 123 contains a much higher percentage of conventional clay than does P.C. 13, the former absorbs less moisture at all humidities below 93 per cent, as will be seen from figure 5. At this humidity, corresponding to pF 5, the curves cross,

TABLE 2
Relation between diameter of particles and their summation percentages for two soils

DIAMETER	pF	SUMMATION PERCENTAGES		RELATIVE HUMIDITY
		P.C. 13	P.C. 123	
<i>cm.</i>				<i>per cent</i>
.006	2.22	93.4	98.0
.004	2.40	89.5	98.1
.002	2.70	88.0	97.9
.001	3.00	79.0	97.0
.0008	3.10	77.0	96.8
.0005	3.30	73.0	96.0
.0002	3.70	58.8	90.9
.0001	4.00	56.9	87.9	99.5*
.000043	4.37	48.6	74.7	97.0
.000023	4.64	46.2	59.0	96.5
.000016	4.80	45.0	49.8	95
.0000094	5.03	45.7	39.2	92
.000001	6.00	40.0	12.0	40
.0000001	7.00	0

* Calculated from the formula:

$$\text{pF} = 6.5 + \log_{10} (2 - \log_{10} h)$$

where h is relative humidity.

and at higher humidities P.C. 123 absorbs more moisture than does P.C. 13. It will be seen that pF 7, which corresponds to the oven-dry state, also marks the lower limit of the colloidal state (particles of diameter 10^{-7} cm.). It is interesting to note that particles of diameter 10^{-7} cm., corresponding to pF 7, will have a capillary diameter of the order of 3×10^{-8} . The diameter of water molecules is of the order of 3.45×10^{-8} . In other words, the particles of this size will be packed so closely that even a single molecule of water could not be squeezed into the interspace. Such colloidal particles can render a soil completely impervious to water. The sodium carbonate method of lining canals and water courses for preventing seepage losses, devised by the writer (4), is based on this principle. It aims at converting a Ca-soil into a

Na-soil; the latter being highly dispersed fills the interstices with colloidal particles, leaving very little space for the water to pass through. It is significant how the colloidal state in soils merges into the molecular state. It is therefore not difficult to understand that many of the so-called adsorption phenomena in soils may be essentially of a chemical nature and in no way different from similar reactions in molecular dispersions, i.e., solutions.

The extreme limit of conventional clay, i.e., particles of 0.0001 cm. diameter, corresponds to pF 4, which is equivalent to a relative humidity of 99.5 per cent. Particles of larger diameters therefore give capillaries that are too coarse to be filled through the vapor phase. This explains the often quoted fallacy that it is not possible to saturate a soil completely from a fully saturated atmosphere. It is also clear that the region of hygroscopicity lies below the

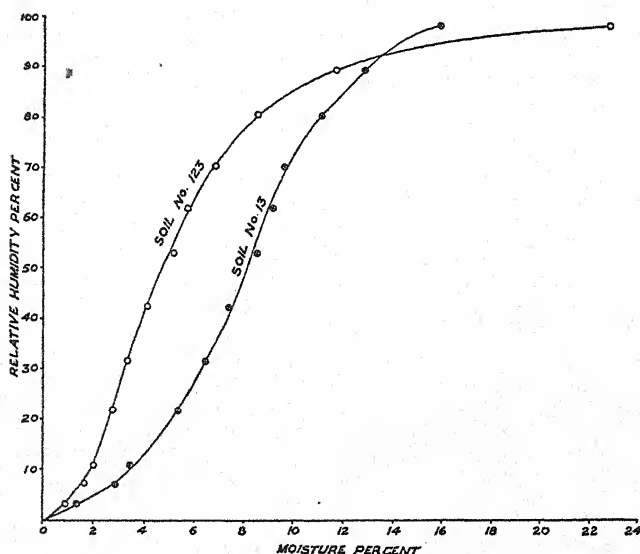


FIG. 5. RELATION BETWEEN MOISTURE CONTENT AND RELATIVE HUMIDITY IN TWO SOILS

conventional clay, and an explanation of the varying hygroscopicity of clays lies in the size distribution of the ultraclay particles. A semiquantitative relation between conventional clay and hygroscopicity is also apparent from these considerations. A general similarity in the shape of the mechanical analysis summation curves and relative humidity moisture content curves can also be understood. This similarity would be still more striking if we could compare the ultramechanical analysis of particles smaller than the conventional clay.

We have seen that a sand consisting of particles of 0.01 cm. diameter requires a suction pressure of the order of pF 2 to overcome the surface tension of the water held in the capillaries. We can therefore vary the pF from 0 to 2 without altering the moisture content. For a finer sand, say 0.001 cm.

diameter, the suction force must exceed pF 3 before any water can be drawn out. It is clear, therefore, that there must be an abrupt drop in the pF -moisture content curve. In soils, this abrupt drop is masked by secondary effects, and as the pressure deficiency is increased, some water is yielded at every step. We shall therefore endeavor to visualize the cause of this apparent anomaly. The phenomenon of swelling of soil on absorbing water is well known, but its mechanism is not quite clear. We are generally content with the statement that water somehow can make room for itself by separating the particles a little from one another. The real situation can be very well imagined if we recall the property of "auto-disintegration," by virtue of which soil colloids go into suspension without being shaken (5). We can imagine the larger interstices between compound particles as being just filled with water. This is followed by the auto-disintegration of colloidal clay, which is accompanied by an increase in volume, because the particles that were originally most closely packed are no longer so. In the end the capillaries are filled not with water but with a highly viscous fluid constituting a clay suspension of great density. In the extreme case the bigger particles can float in this suspension, and the entire mass becomes plastic. If suction is applied at this stage, water filters out and the volume decreases correspondingly. This continues until the soil aggregates are most closely packed. That this might be a true picture of the swelling of soils is supported by the fact that this phenomenon is most pronounced in Na- and Li-soils, the colloidal clays of which are known to impart to the soil the property of auto-disintegration. The yield of water from a saturated soil by suction, therefore, is due to the filtration of water from the clay suspension held in the interstices, and the force required is used in overcoming the elastic rigidity of a thick suspension. The relation between pF and moisture content in this region is, therefore, not real and is due to the capillaries being full not with water but with a clay suspension. The absorption and removal of water from a soil is a slow process, and the attainment of equilibrium may take several days. An interesting experiment may be cited to illustrate this phenomenon. If to a saturated sand column held under a pressure deficiency some water is added, the whole of that water passes on to the burette tube of the capillarimeter. If the soil is held in a large Büchner funnel and water is added drop by drop, the only visible effect is a rise of water in the burette tube exactly equal to the volume of water added. On the other hand, if the experiment is repeated with soil, the water may take several days to pass on to the burette tube, and even then some of it may be retained in the soil. This part goes to swell the soil mass. Similarly, soil may continue to yield water for several days under a certain pressure deficiency. It is for this reason that determination of a true volume for the capillary pull of soils is difficult. Even the approximate values leave no doubt, however, that the forces involved are the same both in sands and in soils.

It must be emphasized that the process of emptying the capillaries is dis-

continuous. A certain critical pressure deficiency is required to overcome the surface tension. The relative humidity-moisture content curves show no discontinuity because there is no discontinuity in the size distribution. The equilibrium moisture at every vapor pressure merely indicates that the capillaries formed by particles up to a certain limiting size are full, and the capillaries in the larger sizes are empty. When the vapor pressure is lowered, another set of capillaries corresponding to a lower size are emptied.

This view gives a new orientation to our concept of the wilting coefficient of soils. The fact that the wilting coefficient of soils is of the order of pF 4.2 (5) is likely to give an erroneous idea of the mechanism of moisture absorption by root hairs. For instance, it would seem that the limiting factor was the suction pressure of the soil, and a possible connection between the suction pressure of roots and that of the soil might be sought. A moment's reflection will show that this view is likely to be misleading. The limiting factor in the utilization of soil moisture may be not the suction pressure but the limiting size of the root hairs which cannot penetrate capillaries below a certain diameter. The development of the suction pressure in soils is entirely due to the surface tension, and unless a root hair can enter and establish contact with the water surface, the plant cannot take up the moisture. This condition of isolation begins to operate when the moisture has receded to the capillaries formed by particles of 0.0001 cm. diameter corresponding to pF 4. The importance of clay fraction in determining wilting coefficient is at once apparent. Since clay represents only the upper limit of particles of this size, however, the exact relation must depend on the size distribution of finer particles in the clay fraction. Particles coarser than clay are mainly responsible for retaining moisture that is available to plants; clay merely helps in the conservation of this moisture. It might be pointed out that in working out the relation between the capillary pull and the mean diameter of soil particles, the lowest limit of size for calculating the mean diameter was taken as 0.0002 cm., in spite of the fact that there were finer particles which would have reduced the mean diameter considerably. The main contention that emerges from these considerations is that there is a limit to the continuity of the liquid phase when pressure deficiency or suction force is applied to soils. When this force exceeds that required to empty capillaries formed by particles coarser than clay, gaps are created through which transmission of pressure deficiency can not take place. If a wet soil is placed on a dry soil, the suction applied by the latter cannot be transmitted when the soil has been dried to pF 3.3 (field moisture). Although centrifugal force is not limited by similar considerations and it is theoretically possible to reduce the moisture content to any value down to dryness, there are practical difficulties in the production of such an enormous force and we are again limited to a pF value of 3 (moisture equivalent). Plants, on the other hand, through their minute root hairs can reach much smaller capillaries, but it must be emphasized that the limiting factor is not the suction pressure of roots but the size of the capillaries. It is for

this reason that the wilting coefficient must be regarded as a soil characteristic which bears no relation to the suction force of the roots. In fact, it is doubtful whether the so-called suction force of roots plays any part in the intake of water from soils.

In considering the rise and distribution of water in a dry soil through capillarity, a fundamental mistake is made in laying too much emphasis on the vertical height from the free water surface. The whole idea of Buckingham's capillary potential is based on the erroneous assumption that the height of the capillary front is the limiting factor. As a matter of fact, the capillary movement is uninfluenced by gravity and is the same in all directions. In order to visualize the mechanism of the rise of moisture in a dry soil, we must remember that this movement can take place only from larger to smaller capillaries. In other words, a dry soil will only withdraw moisture from a wet soil if the former contains some capillaries smaller than the largest ones in the latter which may be full of water. Each layer of dry soil therefore draws water from the wet layer next to it, and the mean diameter of particles responsible for this pull becomes smaller and smaller as the distance from the free water increases, until the capillaries required for exerting the pull are so small that they are unable to establish contact and the visible movement stops. We have thus a sharp line dividing the wet and the dry soil. The total height of the capillary moisture attained in this way bears no relation to the suction force of the soil except qualitatively. It is, however, related to the size distribution of particles which determine the size of the capillaries. The moisture gradient is governed by the height of the capillary column only incidentally. The free energy due to height has no meaning in this case, and any section of the tube could be cut off and turned upside down without altering the moisture distribution. The lowest moisture content at the highest point is not due to the fact that water is being held against a greater height, but because the thinnest capillaries could not be used to draw out water from the section next to it. The abrupt stoppage of moisture movement is not due to the fact that the capillary force is unable to support a higher water column, but because still smaller capillaries are unable to withdraw water on account of their inability to establish physical contact with the water surface in the larger capillaries. When we speak of the abrupt stoppage of moisture movement, we refer only to the wetness visible as a change in the color of the soil. It must not be inferred, however, that there is no movement of moisture beyond this point. Actually there is, but it is confined to capillaries which are too small to show their wetness. As a matter of fact, this movement is very important in connection with the movement of salts in soils. It can be shown that salts move with water even when the moisture content of the soil corresponds to a relative humidity of 75 per cent or pF 5.6. This movement can be stopped, however, by interposing a layer of sand, the capillaries of which may be too large to draw out water from the finer capillaries in the soil. This principle has been successfully used in preventing salt efflorescence on earth roads in salt areas.

Since the height of a column of liquid supported by capillaries of a given diameter varies directly as the surface tension of the liquid and inversely as the capillary diameter, this relation could be used for comparing surface tensions of liquids other than water. For instance, if Tl is the surface tension of a liquid and Tw the surface tension of water, then:

$$Tl = Tw \cdot \frac{Hl}{Hw} \quad (E)$$

where Hl and Hw are the heights of the capillary columns for the liquid and water respectively. Since Tw is constant and Hw can be kept constant by using particles of the same diameter, (E) can be written:

$$Tl = KHl \quad (F)$$

TABLE 3

Surface tension and interfacial tension values of liquids determined by the capillarmeter, compared with standard values

LIQUID	SURFACE TENSION		INTERFACIAL TENSION	
	Found	Standard	Found	Standard
Benzene.....	34.9	28.9	37.8	35.0
Phenetole.....	32.5	32.7	33.0	29.4
Amylbutyrate.....	29.4	25.2	18.3	23.0
Hexane.....	21.8	18.4	48.8	51.1
Ethyl ether.....	18.3	17.1	10.3	10.7
Toluene.....	38.1	36.1
Oleic acid.....	18.3	15.6
Xylene.....	41.4	37.8
Iso-butylchloride.....	24.2	24.4
Mesitylene.....	33.0	38.7
p-Cyanine.....	31.2	34.6

in which K is a constant characteristic of the grade of sand used. The surface tension values of a number of organic liquids were determined by means of (F), sand of 0.475 mm. mean diameter being used. The results, given in table 3, show a good agreement with the standard values from the International Critical Tables. The experiments were extended to the determination of interfacial tensions between water and some organic liquids lighter than water. These liquids were floated on the water. When the free water surface disappeared as a result of the application of pressure deficiency, the interfacial tension came into play. The break point was as definite as that in the water-air interface. Actually no sand was used in this case. The porous plate of the sintered glass funnel was used for applying the capillary tension. The value of K in equation (F) was 7.335 in the case of interfacial tensions. No particular significance, however, can be attached to this value, which is worked out from the straight line relationship between the capillary height and inter-

facial tension. A comparison of the interfacial tensions determined in this way and standard values, also given in table 3, shows a good agreement. The liquids chosen were those available in the laboratory, and no special care was taken to ensure their purity, as the whole object of the experiment was to illustrate a principle rather than elaborate a method of measuring surface tensions. There is no doubt, however, that the method is capable of refinement and might be employed, with some modification, for measuring surface tensions.

SUMMARY

Evidence is brought forth in support of the capillary tube hypothesis of soil moisture. Determination of capillary force of soils by measuring the maximum height to which moisture can rise, is fundamentally wrong. This can be done only by completely saturating the soil and applying gradually increasing suction pressure until the capillaries break. This force is correlated with the size of particles as demanded by theory.

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Thomas D. Rice

1878-1939

In the death of T. D. Rice, soil science has suffered the loss of one of its active workers. Mr. Rice passed away suddenly at his office on August 23.

He was born at Arredondo, Florida, on April 16, 1878. His boyhood days, for the most part, were spent on the farm of relatives in Randolph County, North Carolina. In 1900 he received the degree of bachelor of philosophy from the University of North Carolina. His major interest was mineralogy, and during his senior year in the university he was an assistant instructor in geology under Collier Cobb.

Shortly after graduation, Mr. Rice accepted a position with the Division of Soils, U. S. Department of Agriculture, at which he stayed until his sudden and untimely death.

During the earlier period of his work in the department, Mr. Rice was in charge of various field parties making soil surveys and special soil investigations in different regions of the country. In 1914 he explored, with H. H. Bennett, the soil conditions in Alaska. In the same year he was promoted to inspectorship and assigned to the West Central States. From that time Mr. Rice, in close association with Dr. Curtis F. Marbut, divided his time between inspection trips throughout the Middle West and the tireless review of numerous soil survey reports.

Only those who were close to him during his life know what a surprisingly large volume of work was done by Mr. Rice during the 25 years of his inspectorship. Several hundred reports passed through his hands. To every page and every line of them he gave his careful attention. All the field data for these reports were examined by him and thoroughly discussed with the field men during the inspection trips. He did his work with amazing patience, never losing his temper and never claiming any credit for himself. The credit was given to the field party; his was only a modest mention in the list of names—"T. D. Rice, Inspector, District 3."

Unassuming, entirely free from selfish ambition, Mr. Rice did not leave many individual contributions to soil science. He generously gave most of his life to the less spectacular but not less important task of helping others to do their parts in exploration, survey, and description of the soils of the United States. In this way he faithfully served soil science for almost 40 years.

He entered the field of soil investigation in the United States almost at the beginning of this work and was one of the few pioneers in the field. This group headed by Milton Whitney began their work at the time when soil science was just emerging from its infancy. They organized the investigation,

worked out the method and technic of survey, and developed a system of correlation and classification of soils which gradually became known throughout the world as the American system. At the same time, they had to train the young cadre of field men and to lead and supervise the field work throughout the country. The work progressed rapidly in close cooperation with various state organizations, and from it grew the American School of Soil Science.

Mr. Rice devoted most of his life to the building up of this school. As a charter member of the American Soil Survey Association, which grew into the Soil Science Society of America, he had a particular, almost parental interest in that organization. He did not miss a single meeting and gave much of his time and energy to its development. Sometime a historian of this period of development of soil science undoubtedly will mention many men who contributed to its progress. He will mention Whitney, Marbut, Lyon, Emerson, Shaw, and others. Mr. Rice's name may not appear in the list. This, however, will by no means obscure or diminish the value of his contribution to the collective work.

Modest and rather shy in his life, genuinely unassuming in his work, Mr. Rice persistently avoided being in the front row of the various organizations and societies of which he was a member. In spite of his rare experience and thorough knowledge of soils, he was eager to learn rather than to appear in the rôle of a teacher. A friendly, somewhat timid smile, a complete lack of ostentation, and a kindly humor were his unfailing characteristics.



THOMAS D. RICE



CHARLES FREDERICK SHAW

Photo by Kee Coleman

Charles Frederick Shaw

1881-1939

Charles F. Shaw, professor of soil technology in the University of California, died at Berkeley, California, on September 12, after a brief illness.

Professor Shaw was born in West Henrietta, New York, May 2, 1881, and was graduated from Cornell University in 1906. That year he served as scientific assistant in the Bureau of Soils, U. S. Department of Agriculture. The following year he joined the staff of the Pennsylvania State College as instructor, and two years later was promoted to the assistant professorship of agronomy. In 1913 he was called to the University of California to a position which he occupied and faithfully filled, except for brief periods of leave, until his death.

Professor Shaw actively prosecuted soil surveys in California throughout his 26 years in the state, and probably no other person had such a complete knowledge of its soils. In addition to carrying on his soil survey work, he headed the division of soil technology and taught soils courses to hundreds of students in the University of California. Professor Shaw took great interest in his students and in student activities and was very popular both with his students and with his colleagues. As leader of the soil surveys and of the division of soil technology, he was pre-eminently successful.

Professor Shaw was widely traveled. He visited and studied soil and agricultural conditions in Australia, New Zealand, Hawaii, and many other regions and countries. In 1930 he was visiting professor of soils at the University of Nanking where he conducted extensive field studies in China and laid the basis for systematic soil surveys later undertaken. The summers of 1926 and 1928 were spent in Mexico in an advisory capacity to the national commissioner of irrigation in teaching and training a corps of men in soil surveying. He served at various times on advisory committees and in field investigations for the U. S. Reclamation Service and other federal and state organizations.

He was a member of the International Society of Soil Science and official delegate of the University of California to the congresses of this society held in Washington, Russia, and England, in the proceedings of which he took active part. He was also an active member of the American Soil Survey Association throughout the period of its existence and played a prominent part in bringing about the consolidation of this association with the Soils Section of the American Society of Agronomy, resulting in the formation of the Soil Science Society of America. He was a Fellow of the American Society of Agronomy, of the American Geographical Society, and of the American

Association for the Advancement of Science, and a member of the American Society of Agricultural Engineers, the Western Society of Soil Science, California Academy of Sciences, Alpha Zeta, and Sigma Xi.

His publications and work are well known, and his influence with students was exceptionally fine. His thoroughness and enthusiasm for soil work were outstanding, and his sympathetic cooperative spirit endeared him to all his colleagues and friends. His loss is keenly felt in California.

W. P. KELLEY

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